

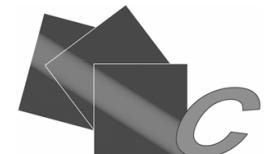
# Characterization of PM<sub>2.5</sub> Using the Raman-SEM

Gary S. Casuccio

RJ Lee Group

Monroeville, PA. USA

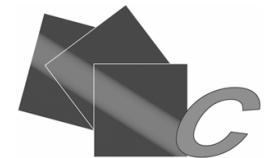
[gcasuccio@rjlg.com](mailto:gcasuccio@rjlg.com)



*RJ Lee Group, Inc.*

# Characterization of PM<sub>2.5</sub> Using the Raman-SEM

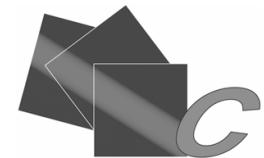
- Authors
  - RJ Lee Group
    - Karen Harris, Steven Schlaegle and Keith Wagner
  - ChemImage
    - John Baker and Mathew Nelson
  - National Energy Technology Laboratory
    - Donald Martello



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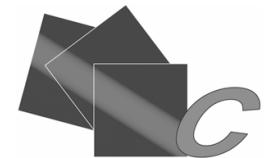
# Characterization of PM<sub>2.5</sub> Using the Raman-SEM

- Acknowledgements
  - Carnegie Mellon University
    - Alan Robinson & Emily Weitkamp
  - RJ Lee Group
    - Traci Lersch



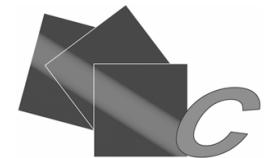
# Characterization of PM<sub>2.5</sub> Using the Raman-SEM

- DOE NETL STTR Project
  - The DOE has funded research related to the development of a hybrid Raman-SEM instrument for the purpose of enhancing characterization of individual particles.



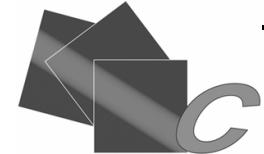
# DOE NETL STTR Project

- The Goal...
  - Combine SEM and Raman technologies to develop instrumentation capable of providing information on the size, shape, elemental composition and molecular structure of individual particles.



# DOE NETL STTR Project Team

- RJ Lee Group
  - Principal Investigator; SEM expertise
- ChemImage
  - Raman instrumentation; Raman expertise
- ASPEX Instruments
  - SEM instrumentation
- Los Alamos National Laboratory
  - Project consultant

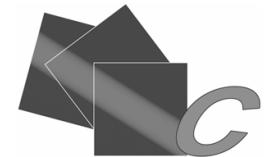


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# DOE NETL STTR Project

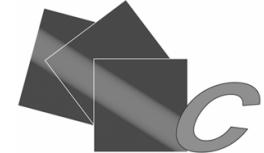
## -High-Risk Technical Research-

- Phase I Feasibility Study
  - Six month study to determine whether feasibility of the approach
  - If successful, prepare proposal for continuation of project.
- Phase II
  - Two year continuation of project
- Phase III

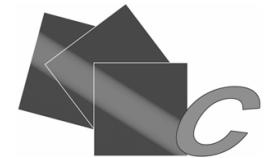


# Phase I Research

- Feasibility of the Raman-SEM
  - Investigations of Bulk Materials
  - Evaluations of Different Filter Media
  - Analysis of Coarse Particles
  - Analysis of Particles Standards
  - Analysis of Ambient Samples

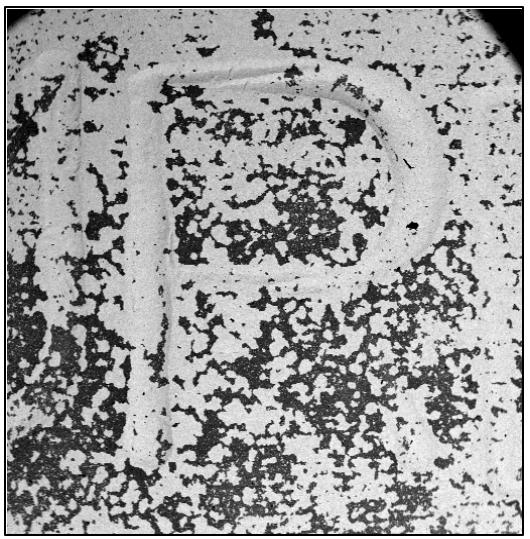


# RJLG SEM Used in Phase I Study

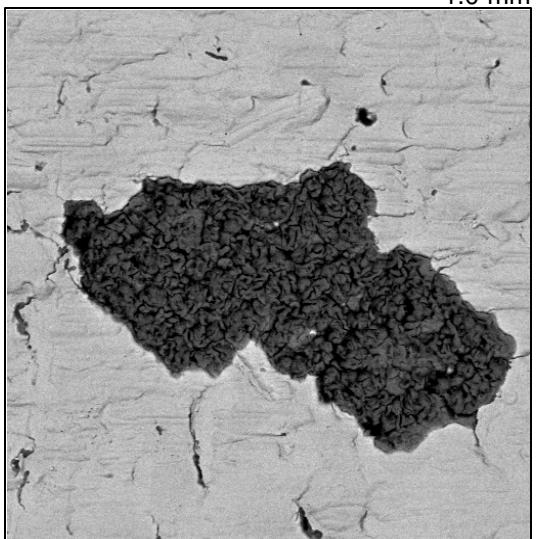


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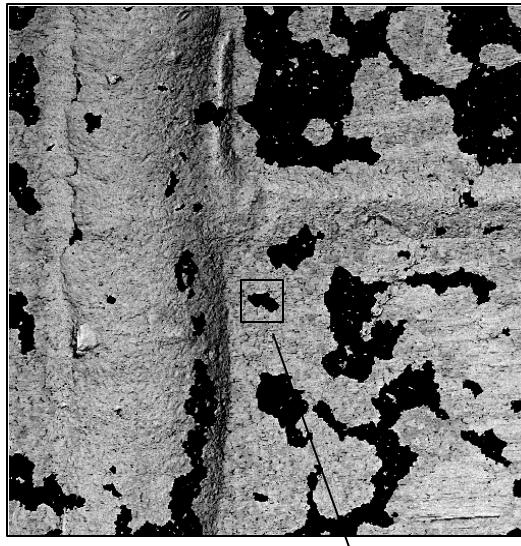
# Surface Corrosion Project



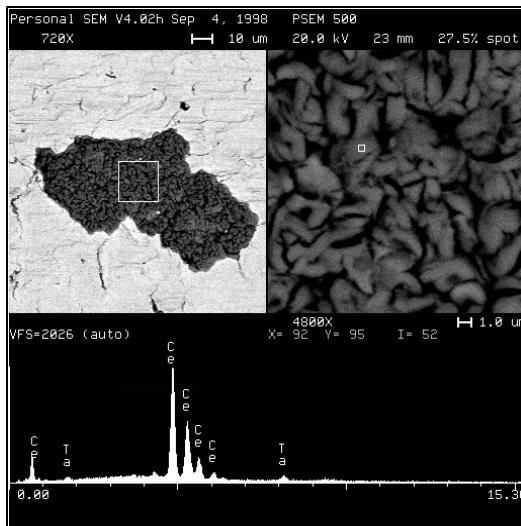
1.0 mm



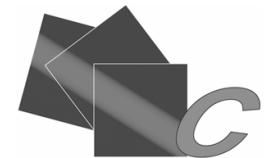
20  $\mu\text{m}$



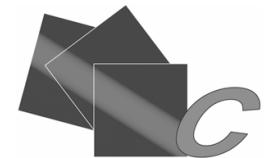
Ce corrosion



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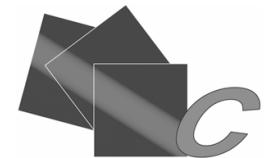
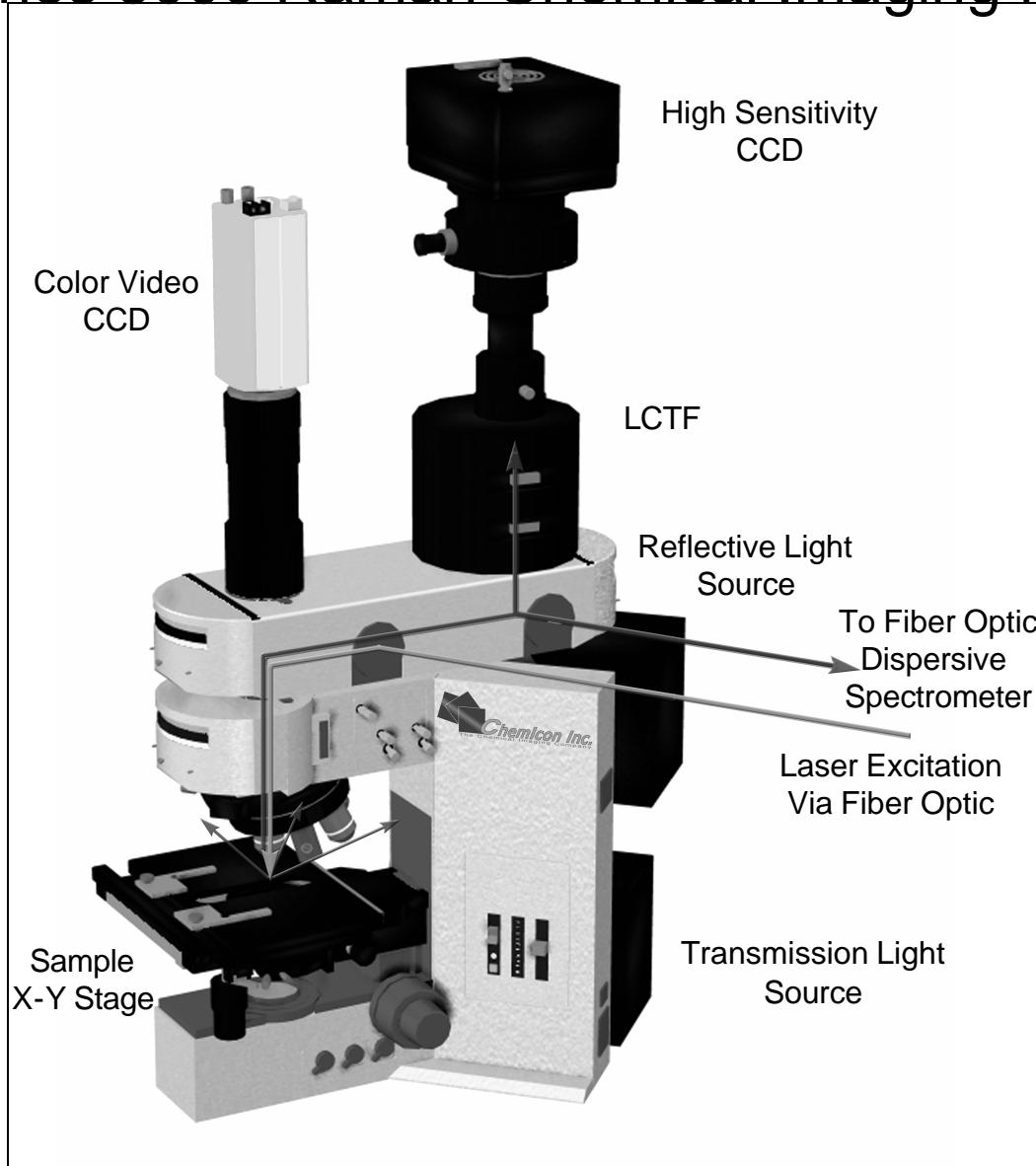


# Falcon Raman Chemical Imaging System



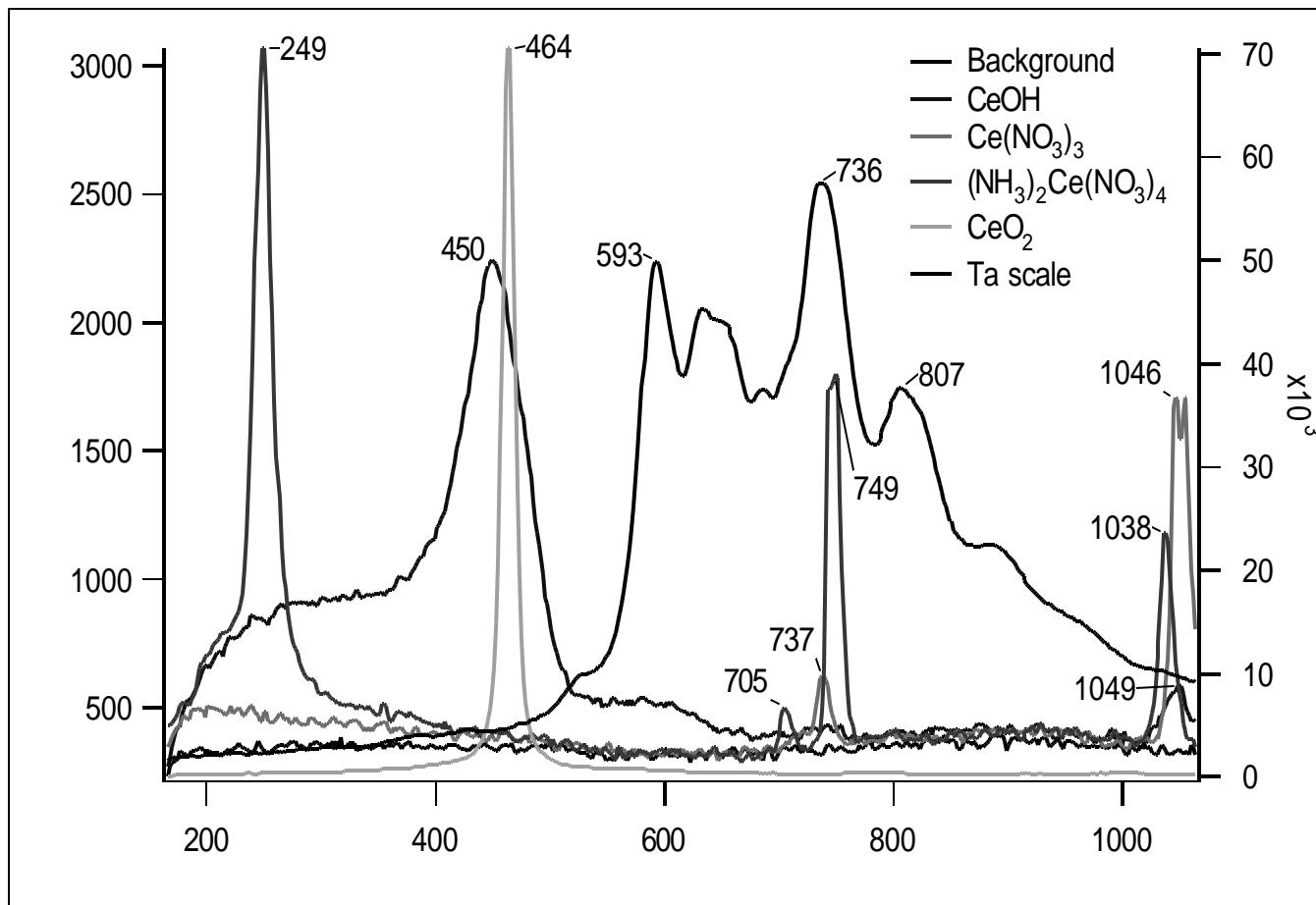
RJ Lee *Group, Inc.*

# Falcon Series 3000 Raman Chemical Imaging Microscope



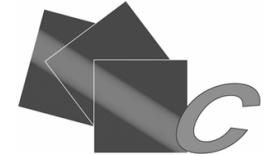
RJ Lee Group, Inc.

# Investigations of Bulk Materials

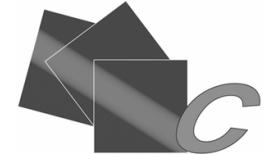
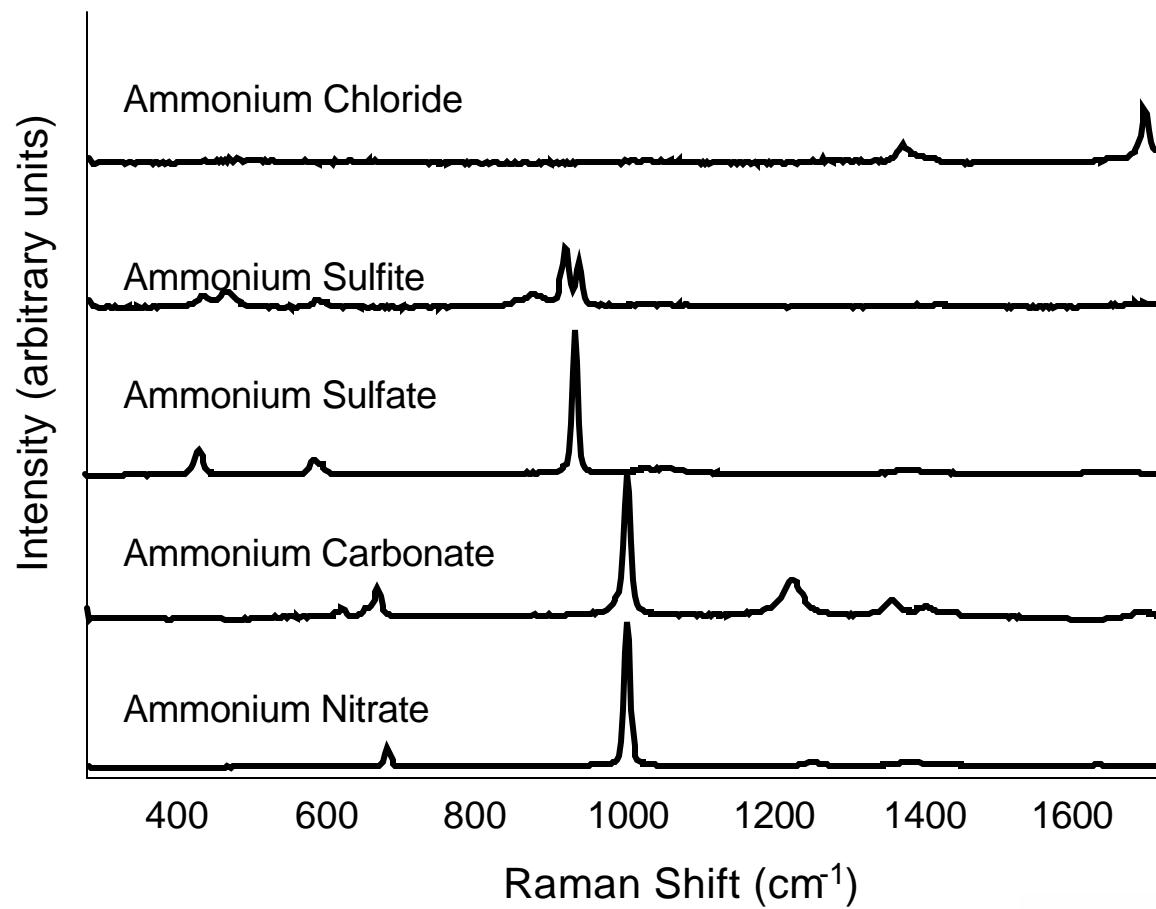


Raman shift ( $\text{cm}^{-1}$ )

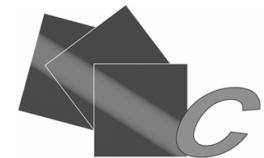
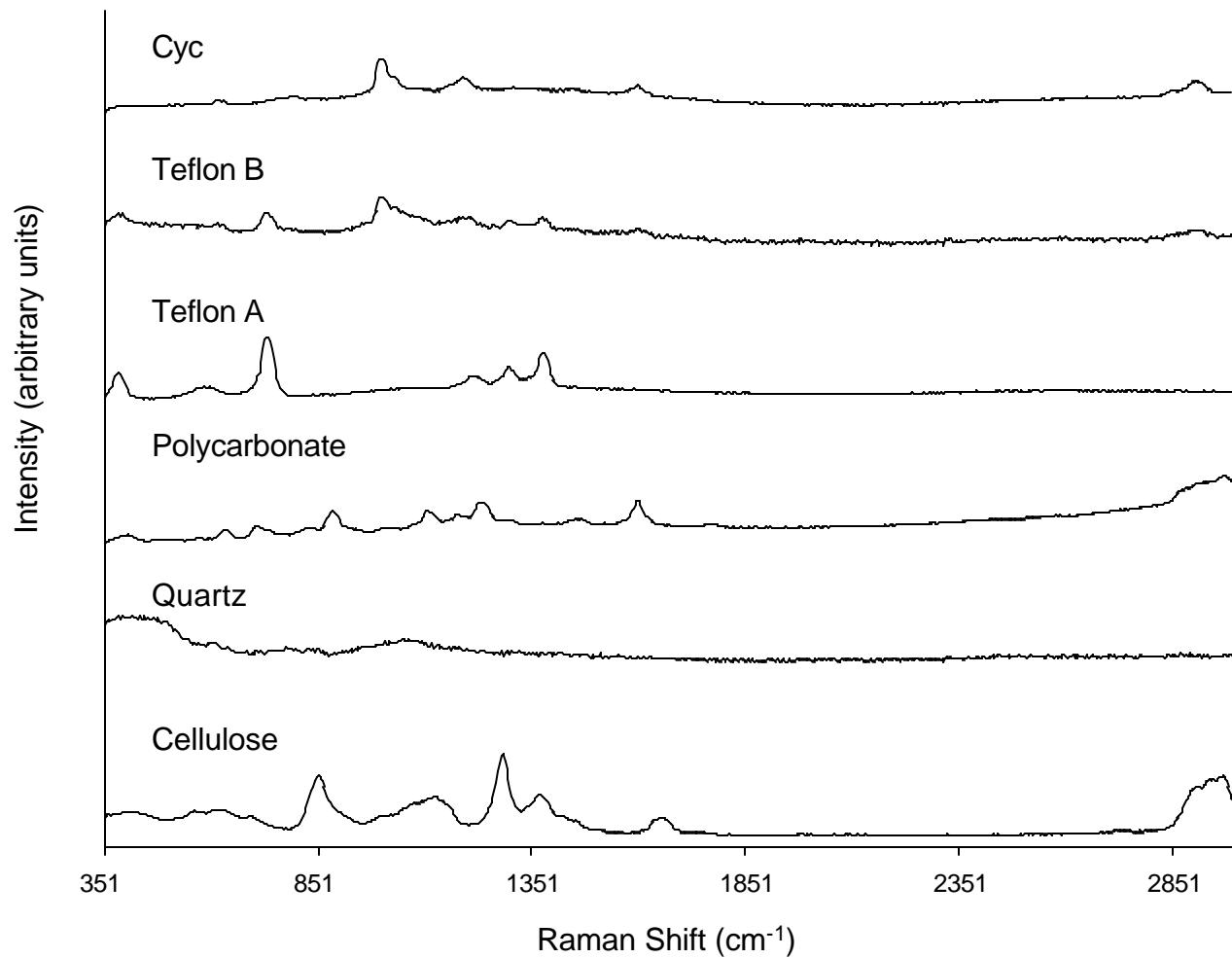
RJ Lee Group, Inc.



# Raman Spectral Library Development



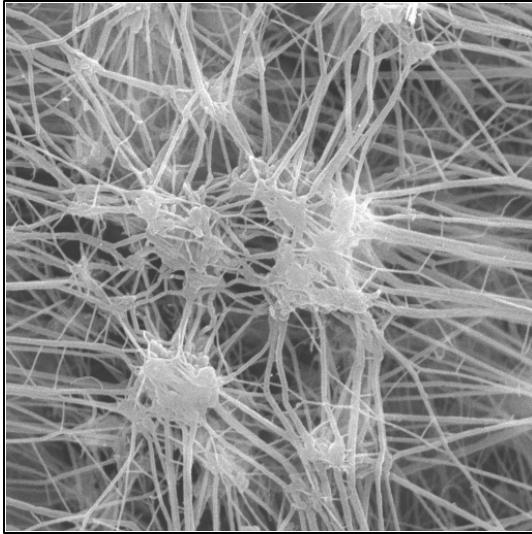
# Dispersive Raman Spectroscopy of Filter Substrates



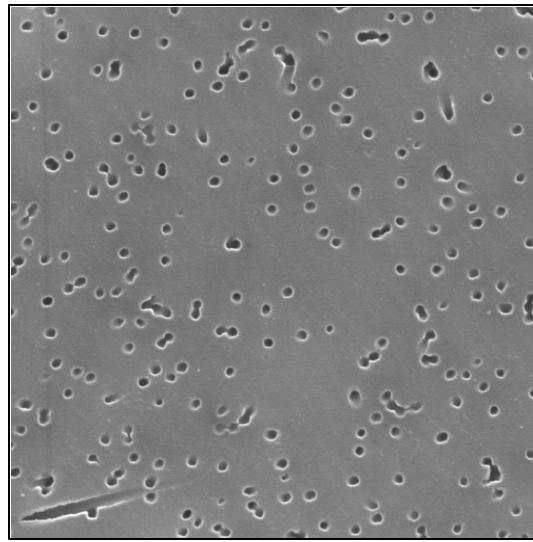
RJ Lee Group, Inc.

# SEM Images Showing Filter Substrate Morphology

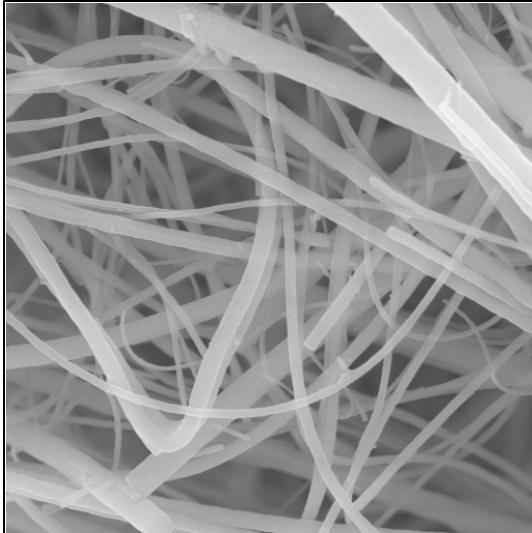
Teflon



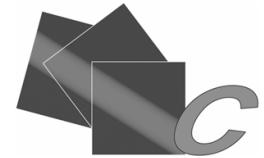
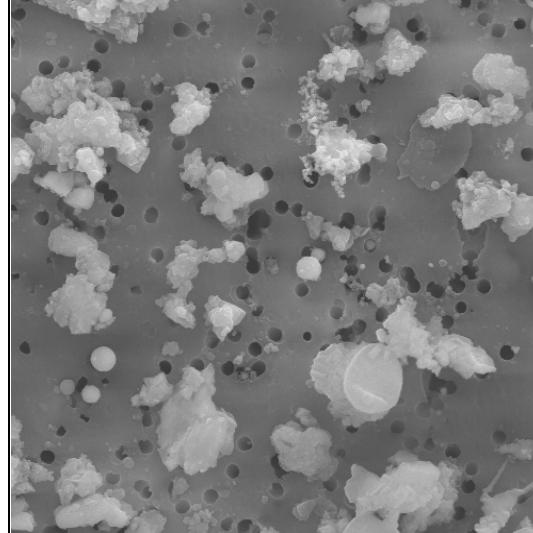
Polycarbonate



Quartz



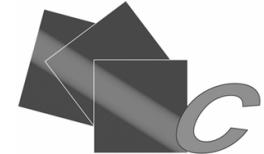
Particulate on  
Polycarbonate



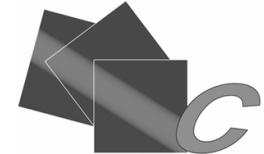
RJ Lee *Group*, Inc.

# Filter Evaluation Conclusions

- Quartz filter is best for Raman spectroscopy analysis due to lack of Raman and fluorescence background.
- Polycarbonate is best for SEM analysis due to smooth filter surface.
- Is polycarbonate suitable for both techniques?



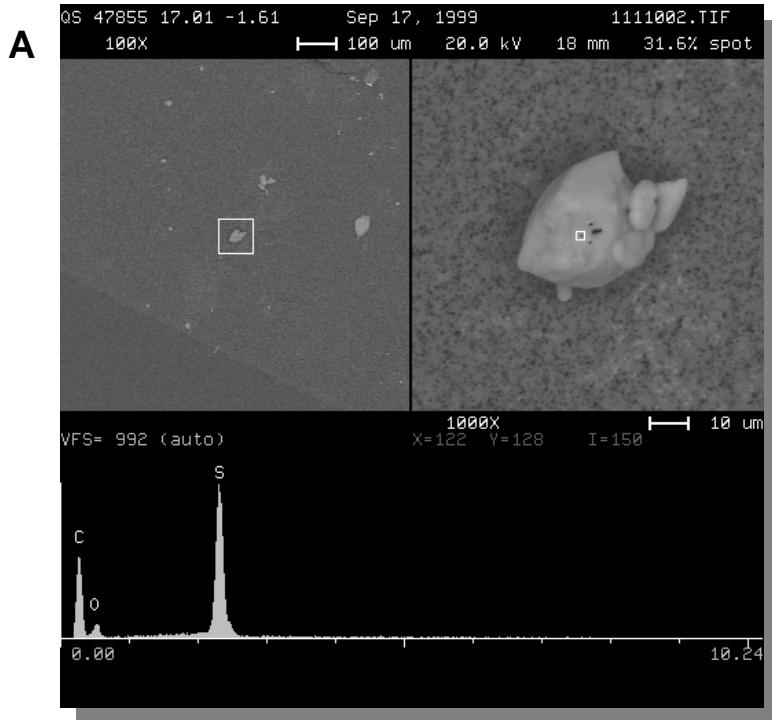
# Analysis of Fine Particle $(\text{NH}_4)_2\text{SO}_4$ and $\text{NH}_4\text{NO}_3$ Standards



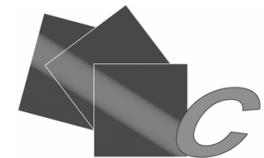
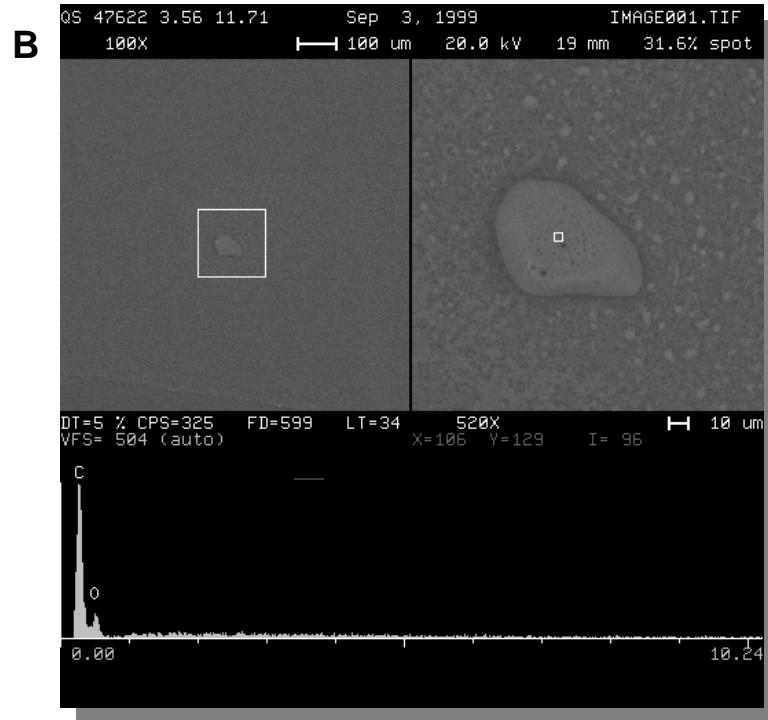
RJ Lee *Group, Inc.*

# SEM/EDS Analysis of $(\text{NH}_4)_2\text{SO}_4$ and $\text{NH}_4\text{NO}_3$ on Polycarbonate Filters

Ammonium Sulfate:  $(\text{NH}_4)_2\text{SO}_4$

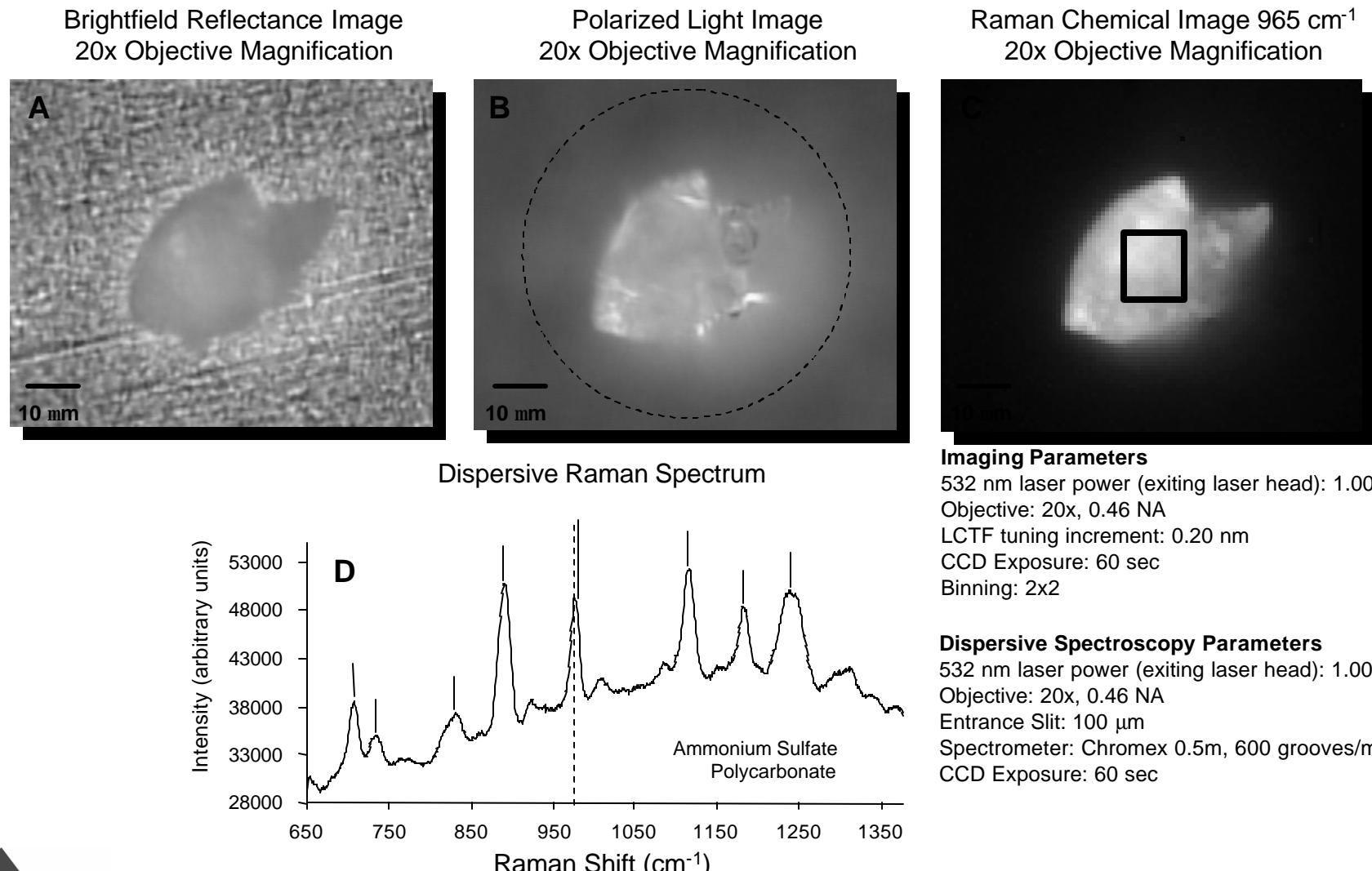


Ammonium Nitrate:  $\text{NH}_4\text{NO}_3$



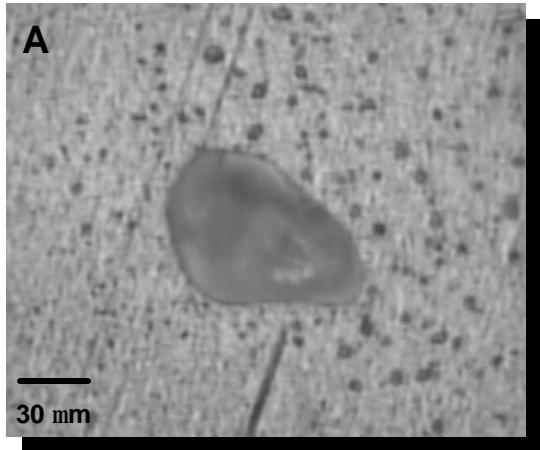
RJ Lee Group, Inc.

# Raman Chemical Imaging of $(\text{NH}_4)_2\text{SO}_4$ on Polycarbonate Filter

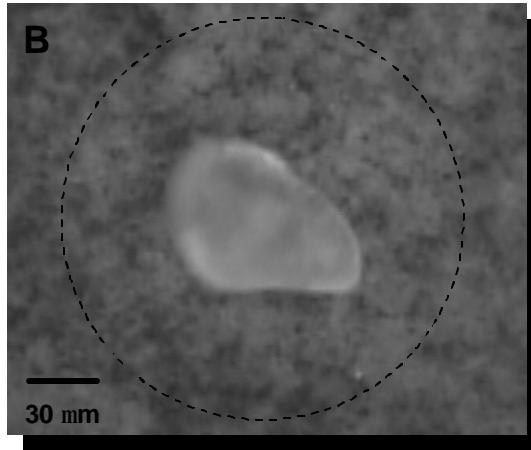


# Raman Chemical Imaging of $\text{NH}_4\text{NO}_3$ on Polycarbonate Filter

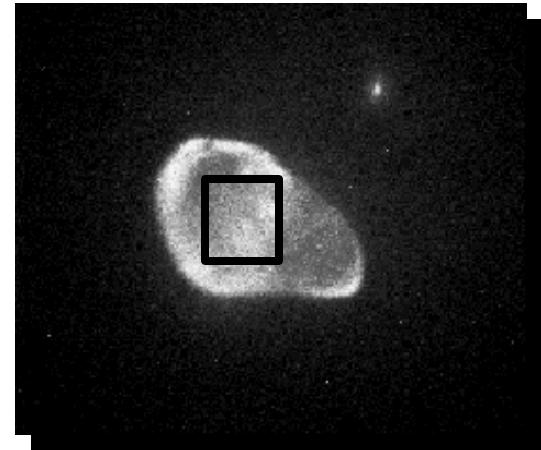
Brightfield Reflectance Image  
20x Objective Magnification



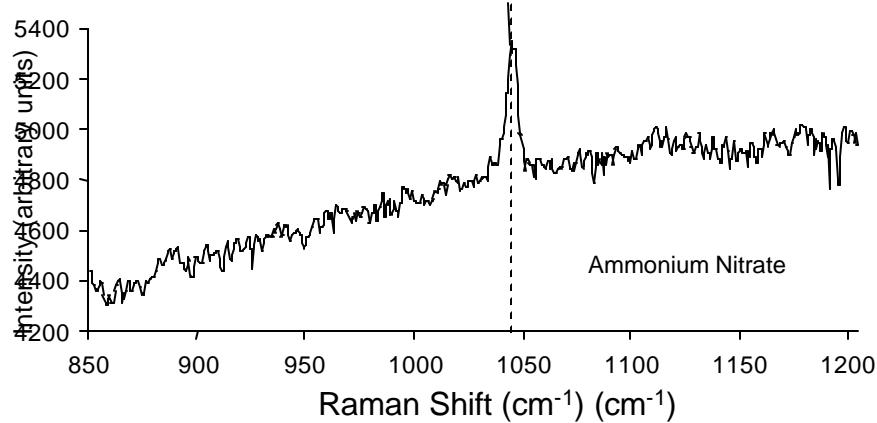
Polarized Light Image  
20x Objective Magnification



Raman Chemical Image  $1041 \text{ cm}^{-1}$   
20x Objective Magnification



Dispersive Raman Spectrum

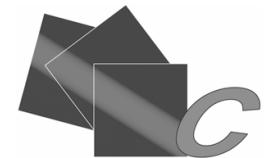


## Experimental Parameters

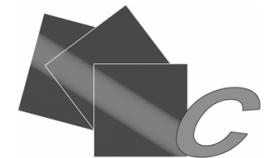
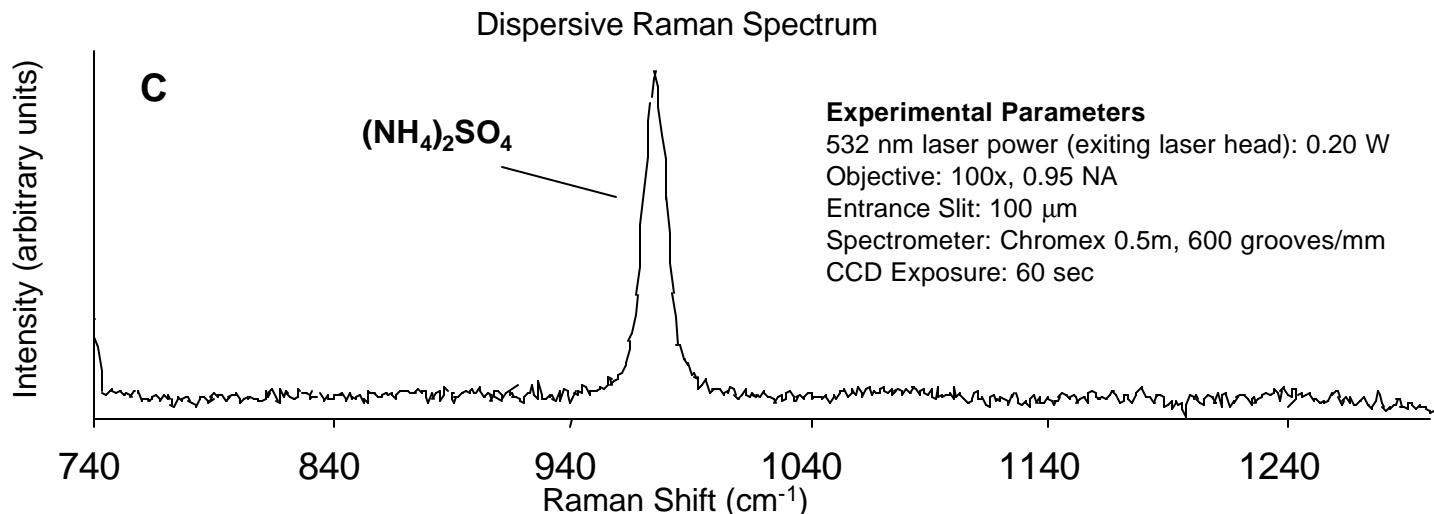
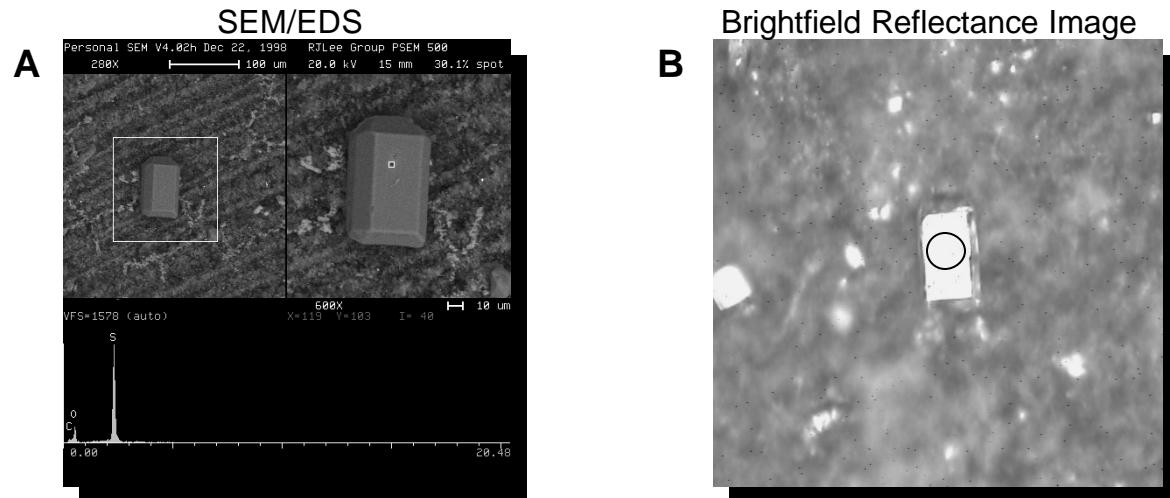
532 nm laser power (exiting laser head): 1.00 W  
Objective: 10x, 0.30 NA  
LCTF tuning increment: 0.10 nm  
CCD Exposure: 60 sec  
Binning: 1x1

## Dispersive Spectroscopy Parameters

532 nm laser power (exiting laser head): 1.00 W  
Objective: 10x, 0.30 NA  
Entrance Slit: 50  $\mu\text{m}$   
Spectrometer: Chromex 0.5m, 1200 grooves/mm  
CCD Exposure: 60 sec / 10 accumulations

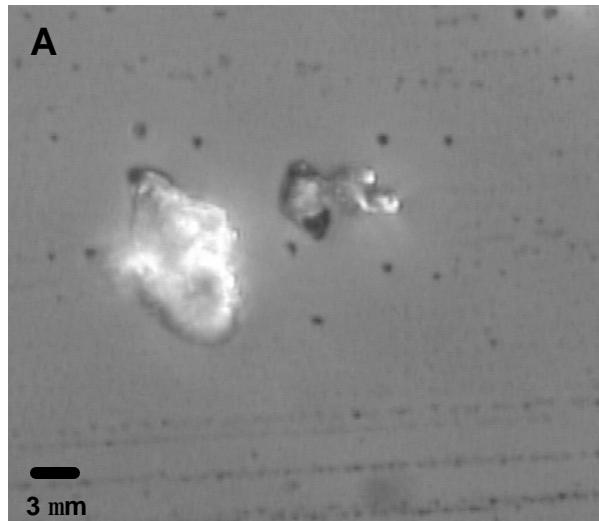


# SEM/EDS Guided Raman Analysis of Ambient $(\text{NH}_4)_2\text{SO}_4$ Particle on Teflon Filter

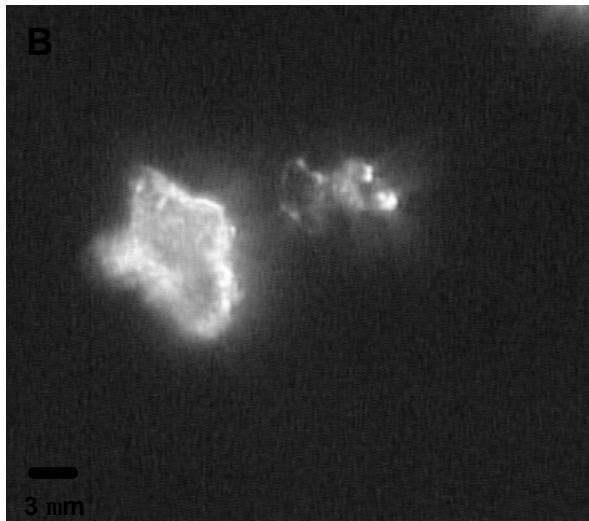


# Raman Chemical Imaging of $(\text{NH}_4)_2\text{SO}_4$ and $\text{NH}_4\text{NO}_3$ Particles

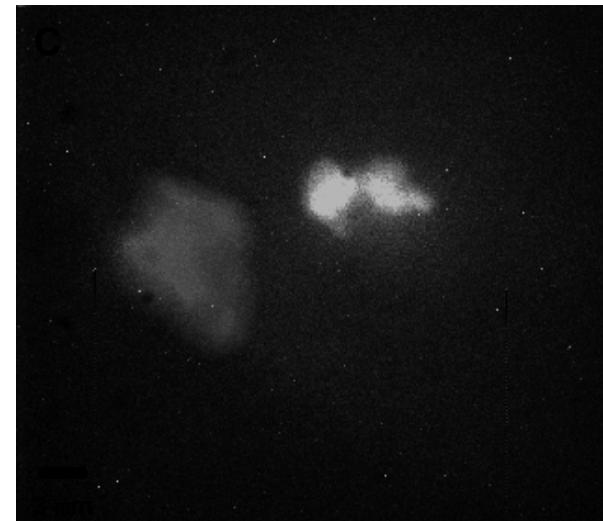
Brightfield Reflectance



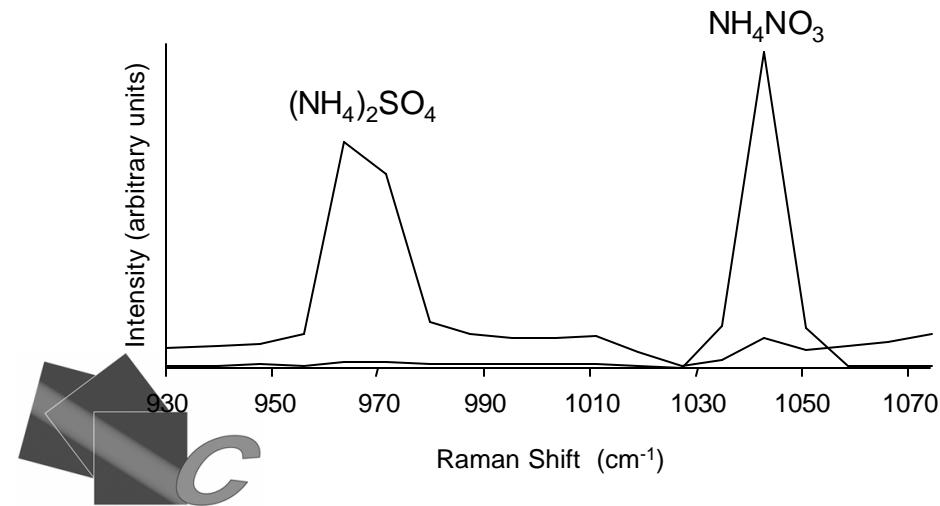
Polarization



Raman Chemical Image

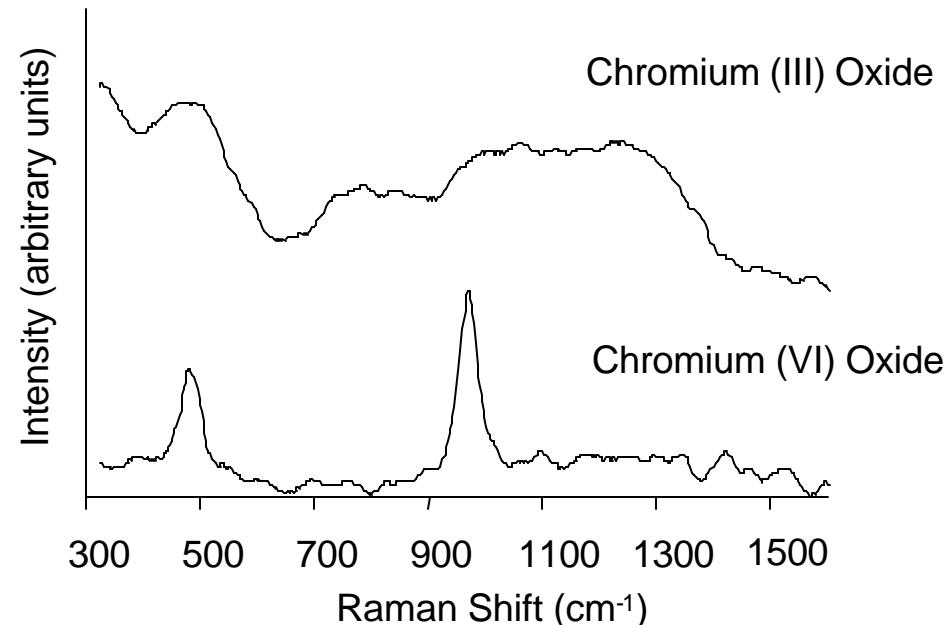
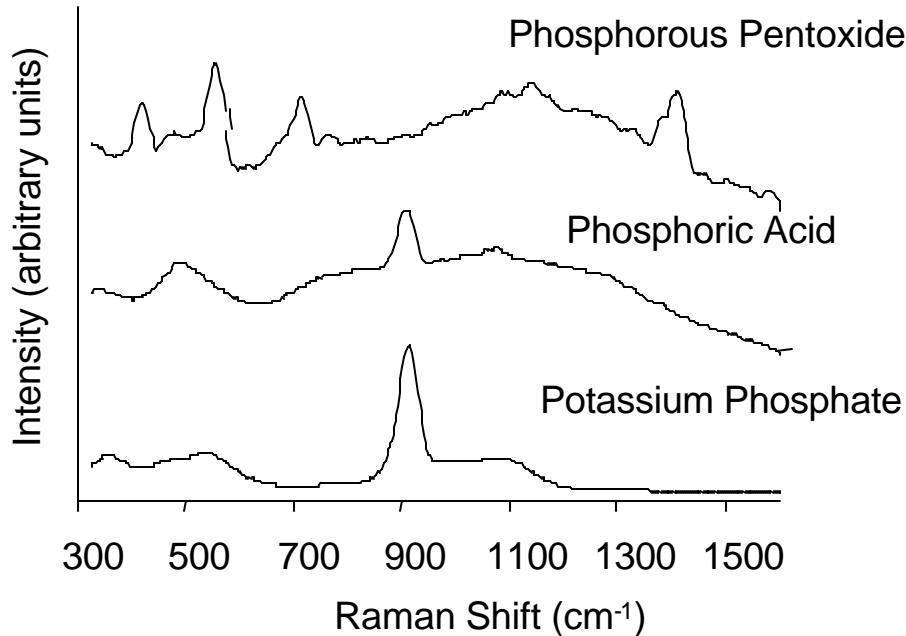


LCTF Raman Spectra



Total Spectra: 89,040  
Sulfate Particle 1:742 spectra  
Acquisition Time: 78 spectra / sec.  
Spatial Resolution: 0.156  $\mu\text{m}$  / pixel

# Dispersive Raman Spectra of Phosphorous and Chromium Containing Compounds

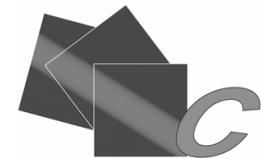


## SAMPLE

- Room temperature (70 °F)
- ## SOURCE
- Millennia II 532 nm Laser
  - Power (at head) = 520mW(PO<sub>5</sub>); 480mW(HPO<sub>4</sub>); 530mW(KH<sub>2</sub>PO<sub>4</sub>)
  - Power (at sample) = 182mW(PO<sub>5</sub>); 168mW(HPO<sub>4</sub>); 185mW(KH<sub>2</sub>PO<sub>4</sub>)
  - Power (at head) = 310mW (Cr<sub>2</sub>O<sub>3</sub>); 100mW(CrO<sub>3</sub>)
  - Power (at sample) = 110mW (Cr<sub>2</sub>O<sub>3</sub>); 35mW(CrO<sub>3</sub>)

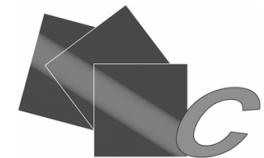
## SPECTROMETER

- Entrance Slit = 20  $\mu\text{m}$
  - Spectrometer = 0.5 m, 150 gr/mm grating
- ## DETECTOR
- T.E. cooled (-40°C)
  - 512 x 768 pixels
  - Pixel size = 24  $\mu\text{m}$  x 24  $\mu\text{m}$
  - CCD Exposure = 5sec(PO<sub>5</sub>); 10sec(HPO<sub>4</sub>); 5sec(KH<sub>2</sub>PO<sub>4</sub>); 10sec(Cr<sub>2</sub>O<sub>3</sub>); 20sec(CrO<sub>3</sub>)
  - Accumulations = 10(PO<sub>5</sub>); 1(HPO<sub>4</sub>); 10(KH<sub>2</sub>PO<sub>4</sub>); 1(Cr<sub>2</sub>O<sub>3</sub>); 1(CrO<sub>3</sub>)



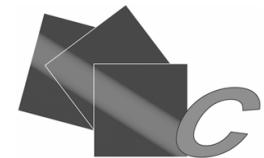
# Summary of Phase I Results

- Demonstrated the potential of the Raman-SEM.
  - Ability to obtain molecular information on individual particles.
- Identified problems associated with the combined analysis.



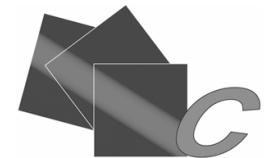
# Problems Encountered Phase I

- Particle relocation difficult using two separate instruments.
- Polycarbonate substrate is not ideal for Raman chemical imaging.
- SEM sample preparation causes problems.
  - conductive coating interferes with Raman.
- Laser damage of particles.
  - sample movement during Raman acquisition

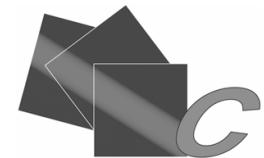


# Phase II STTR Efforts

- Build a prototype Raman-SEM
  - Investigation of anti-charging provisions
- Continued Evaluation of Filter Substrates
- Evaluation of Model PM<sub>2.5</sub> Aerosols

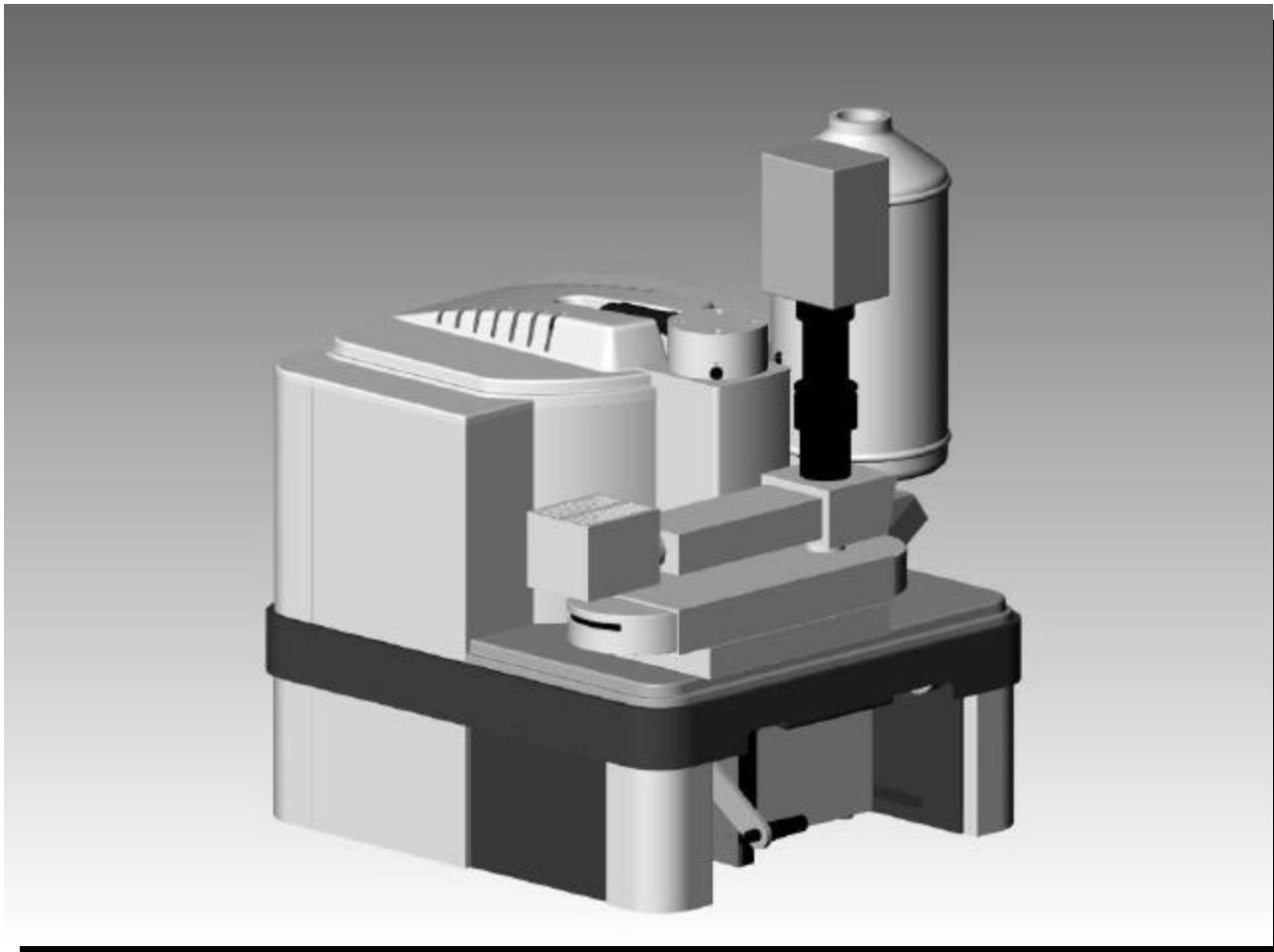


# Prototype Raman-SEM Platform PSEM-2000

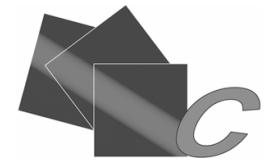


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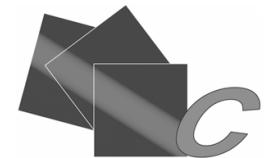
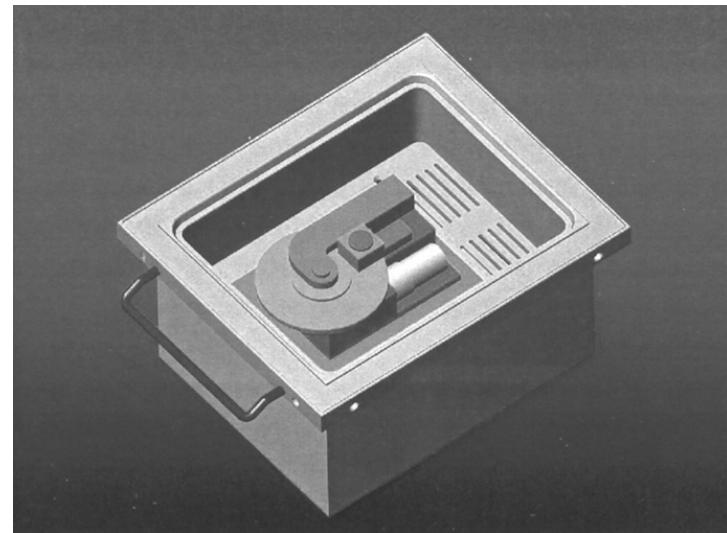
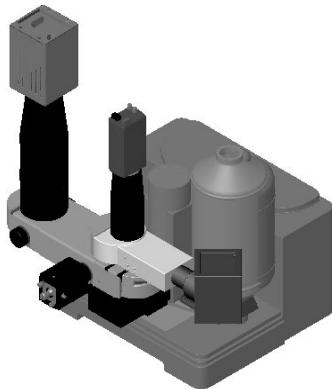
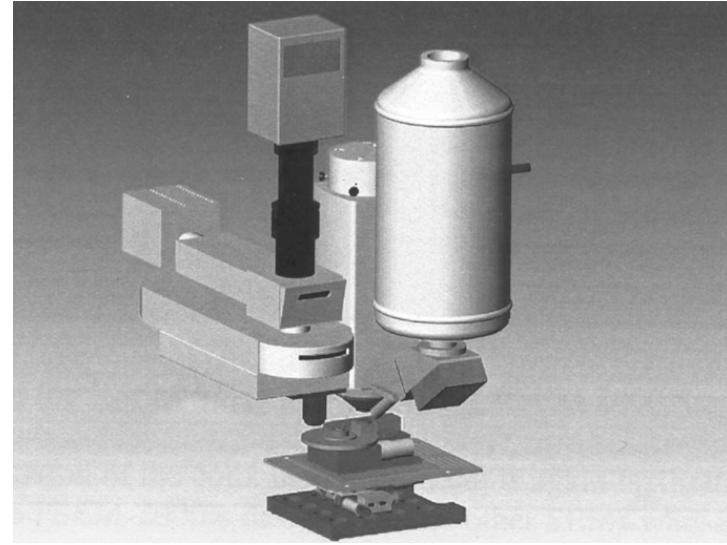
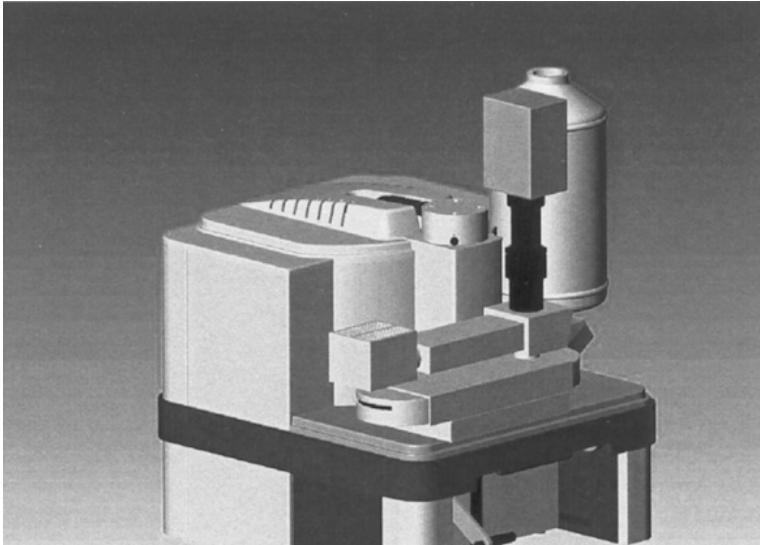
# Prototype Raman-SEM



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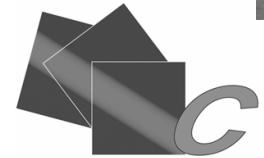
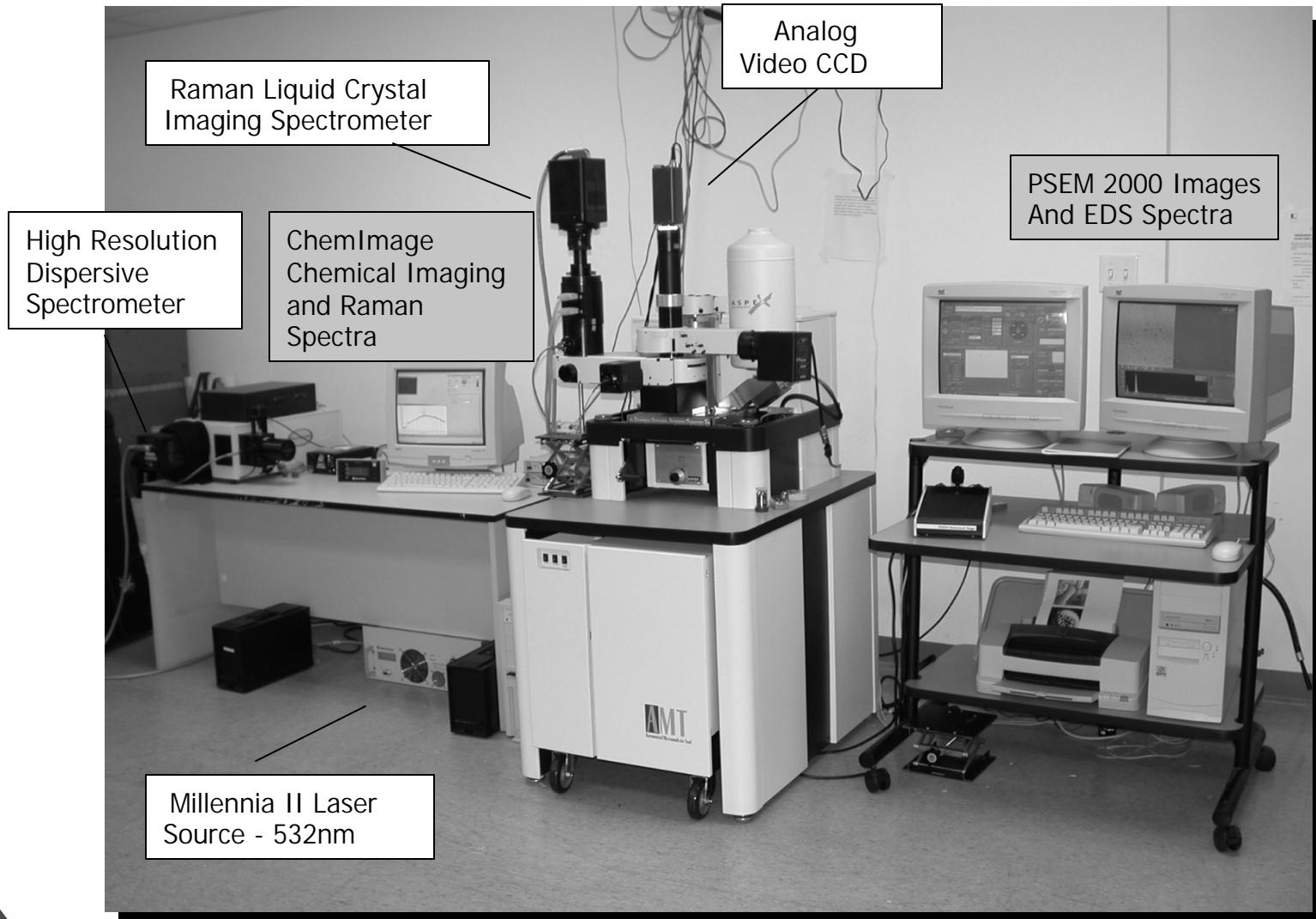


# Raman-SEM Design



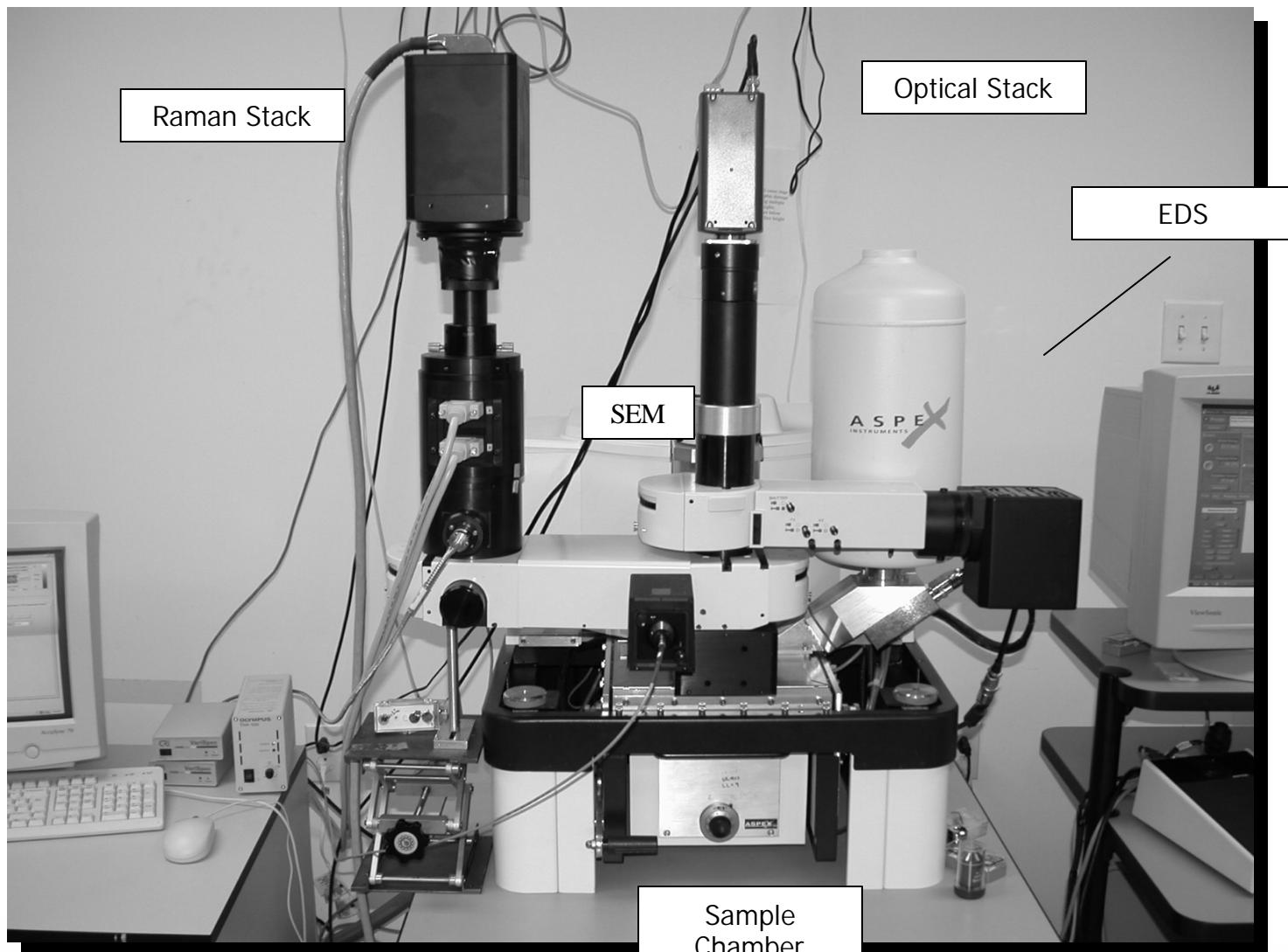
RJ Lee *Group, Inc.*

# Raman-SEM Prototype Instrument

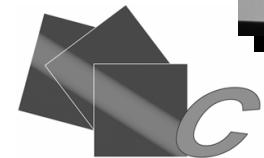


RJ Lee Group, Inc.

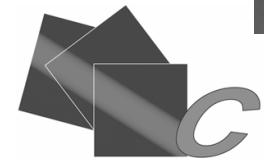
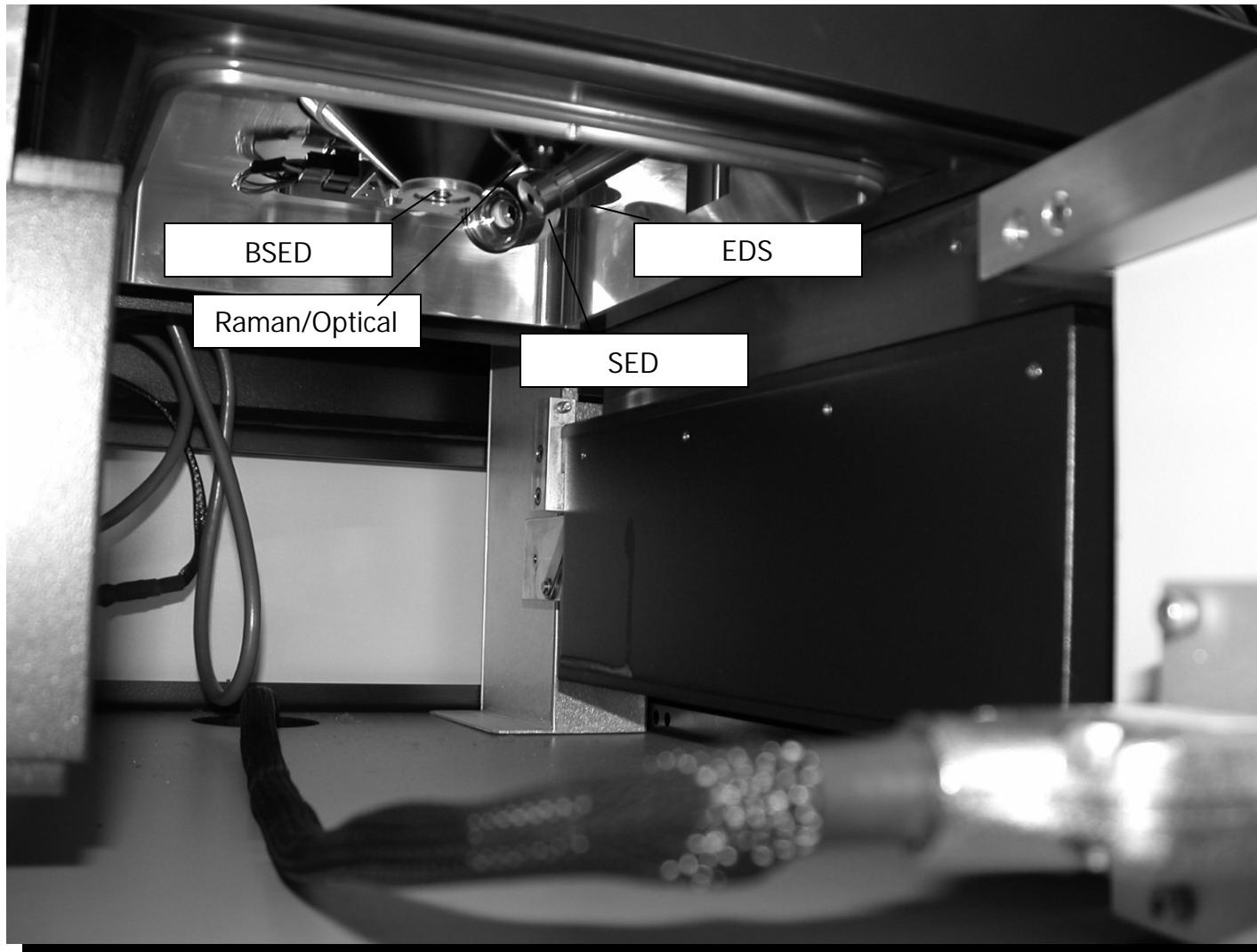
# Raman-SEM Prototype Instrument



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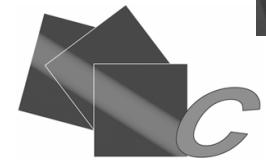
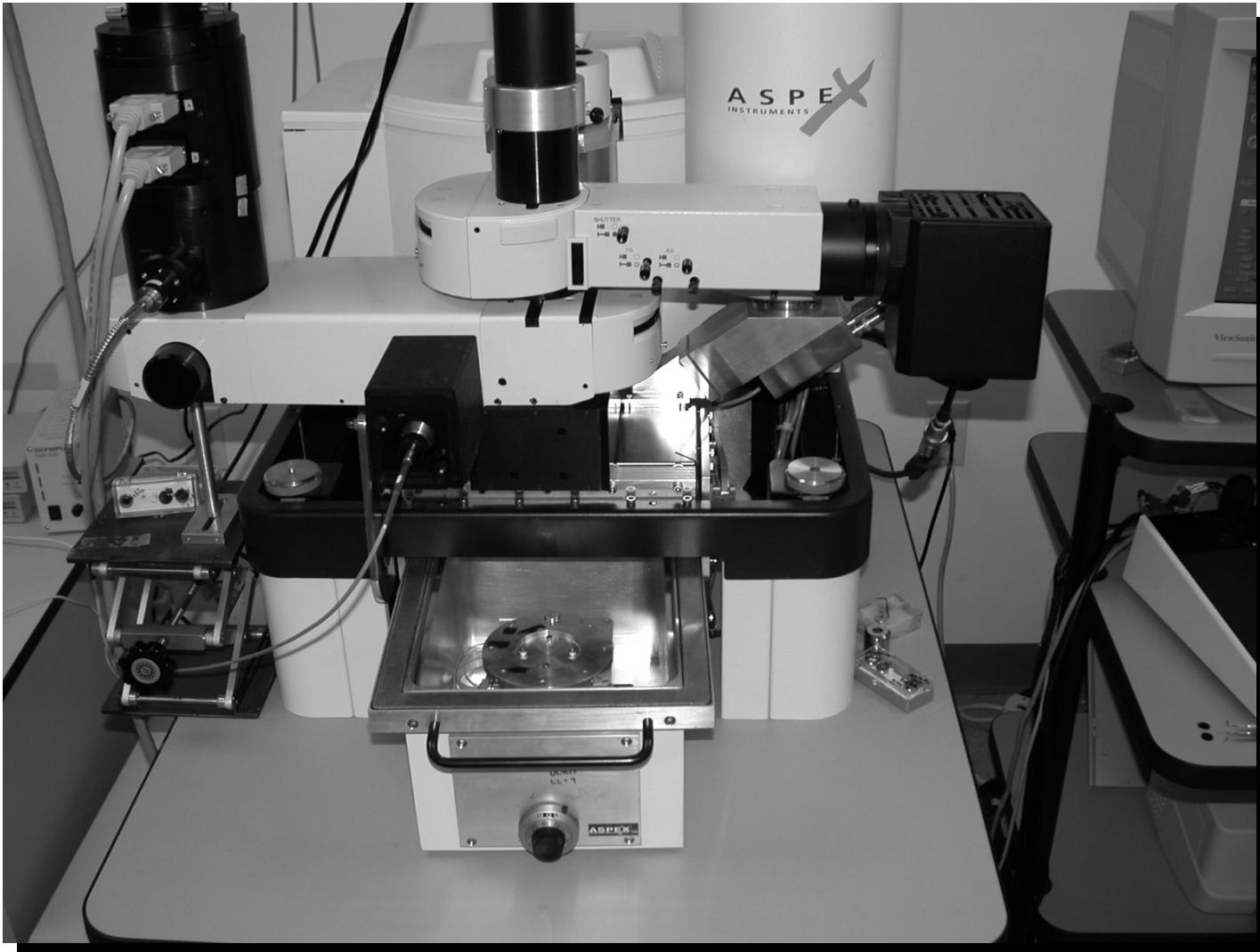


# Raman-SEM Detectors



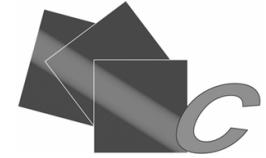
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# Raman-SEM Sample Chamber



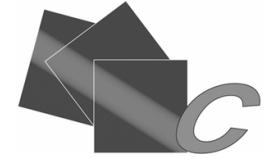
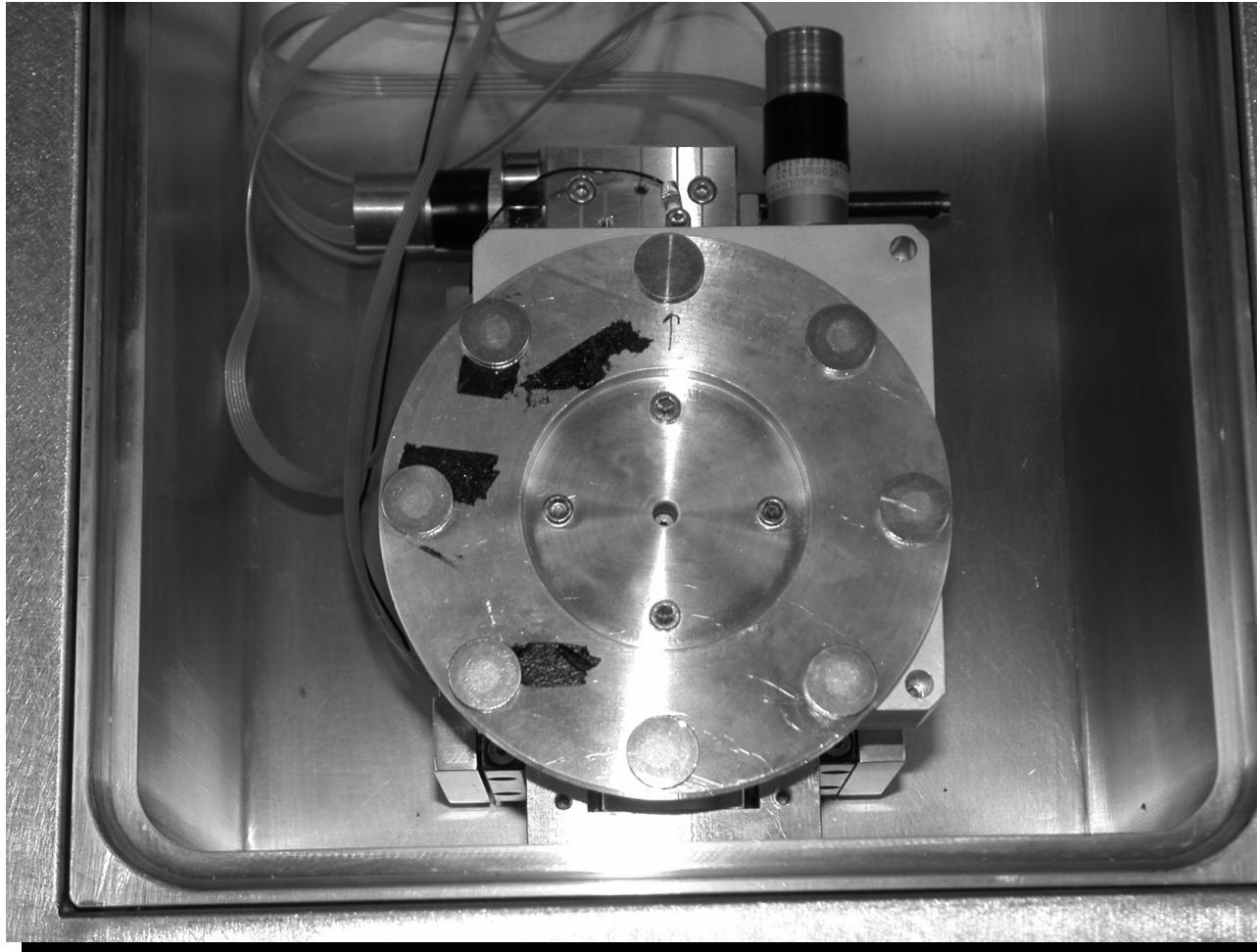
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# Raman-SEM Sample Stage



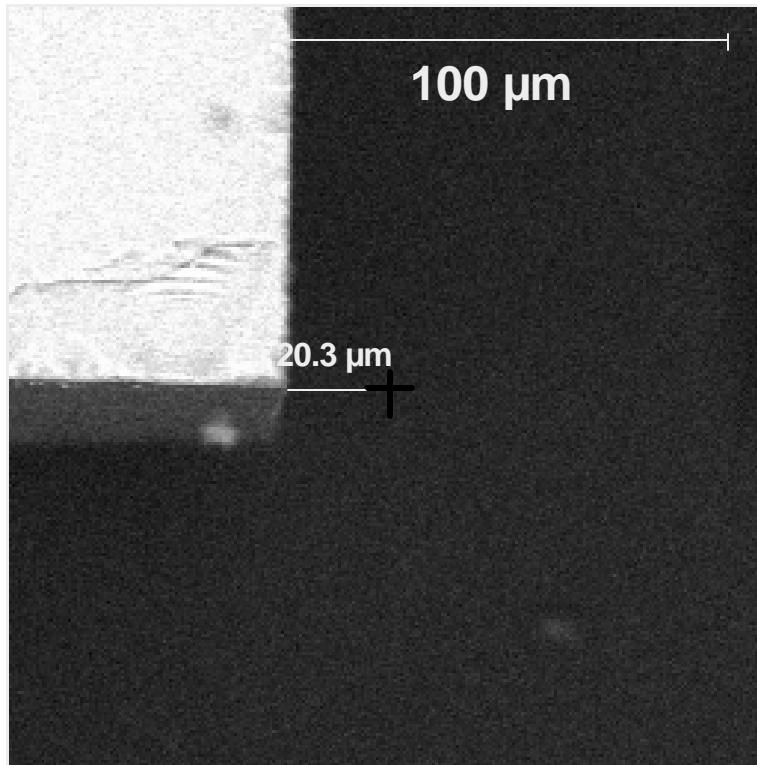
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# Raman-SEM Sample Stage

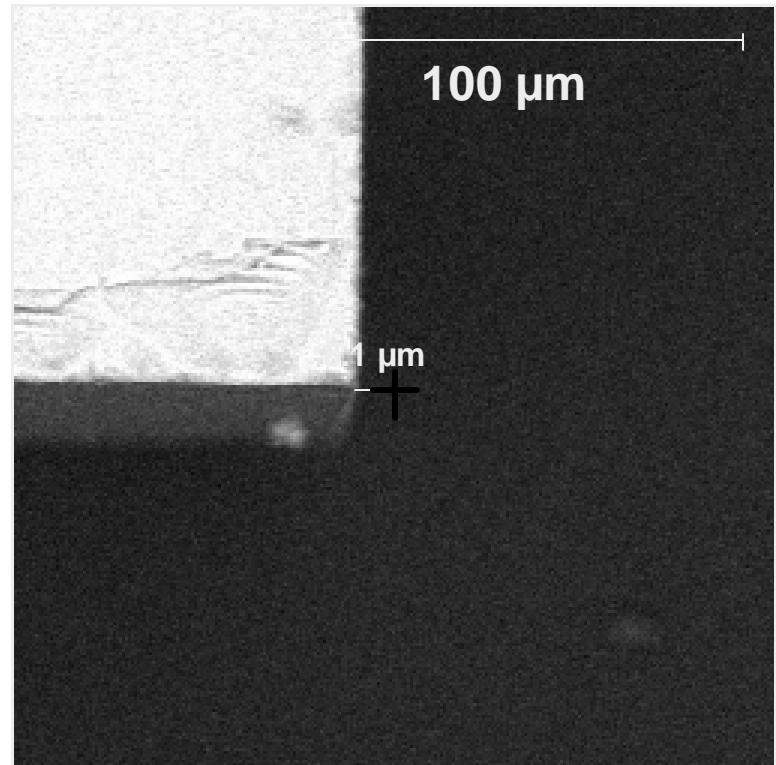


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# Raman-SEM Relocation

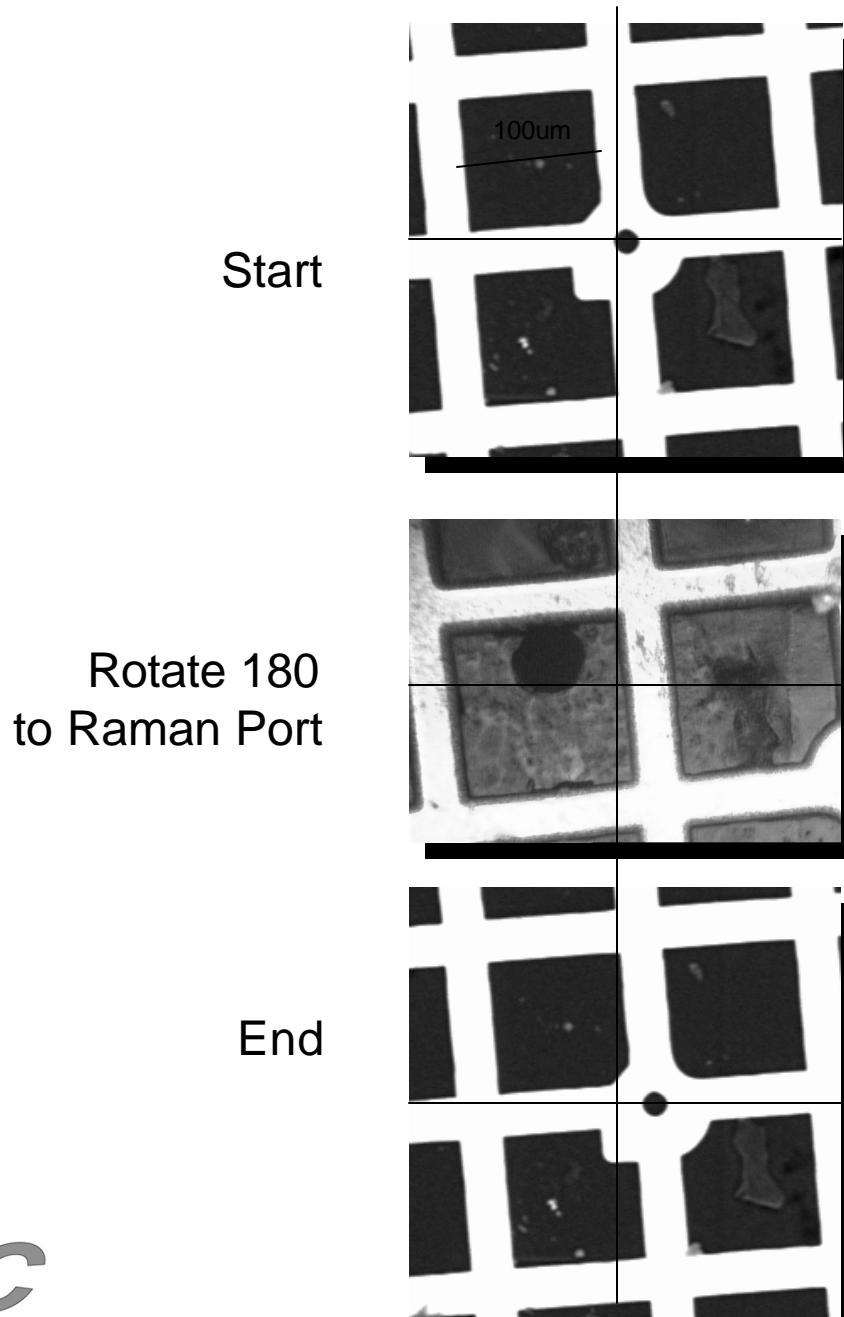


Displacement = 20.3 $\mu\text{m}$



Displacement = 8.1 $\mu\text{m}$

# SEM Stage Reproducibility



## Procedure

1. Center circle of TEM grid in cross hairs
2. Rotate Sample 180 degrees to Raman Port
3. Rotate 180 degrees back to SEM Port

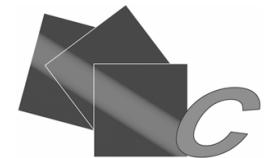
## Conclusions

- SEM had approx  $20 \mu\text{m}$  error
- Translation to Raman port had about a  $100 \mu\text{m}$  error.

Note: Red reference line is center of frame

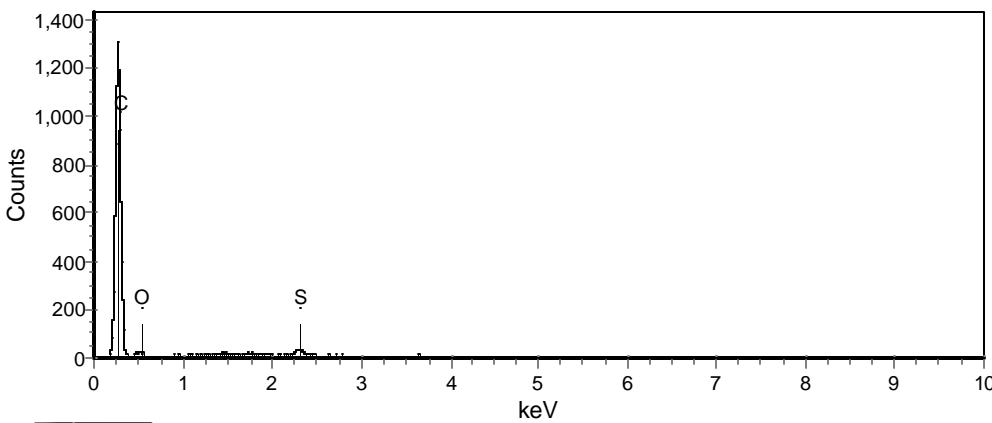
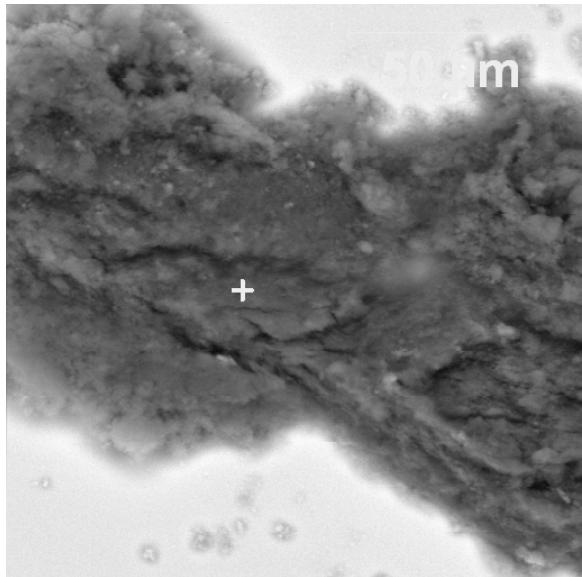
# Typical Experimental Procedure

1. Sample is loaded into RSEM chamber.
2. Objective for Raman analysis is selected and inserted.
3. Sample chamber is placed under vacuum.
4. SEM Analysis: Backscatter Electron Images and EDS spectra are collected.
5. Stage height is carefully set for rotation to Raman.
6. Sample is rotated to Raman side.
7. Region of interest is relocated.
8. Bright field images, Raman dispersive spectra, and Raman Chemical Images are collected.

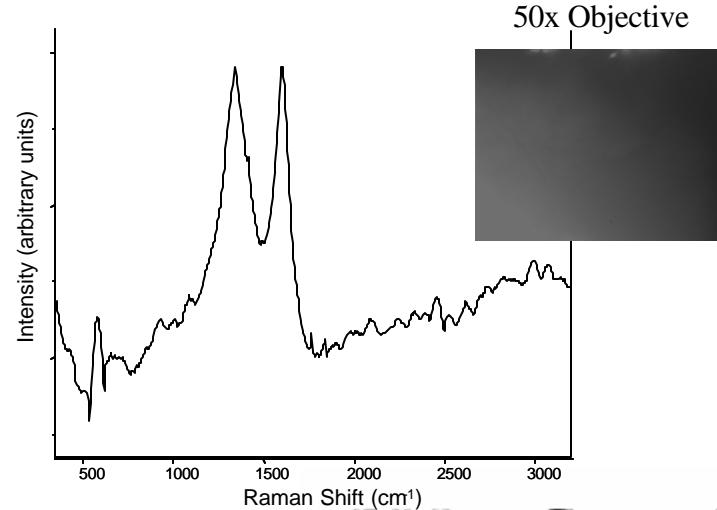
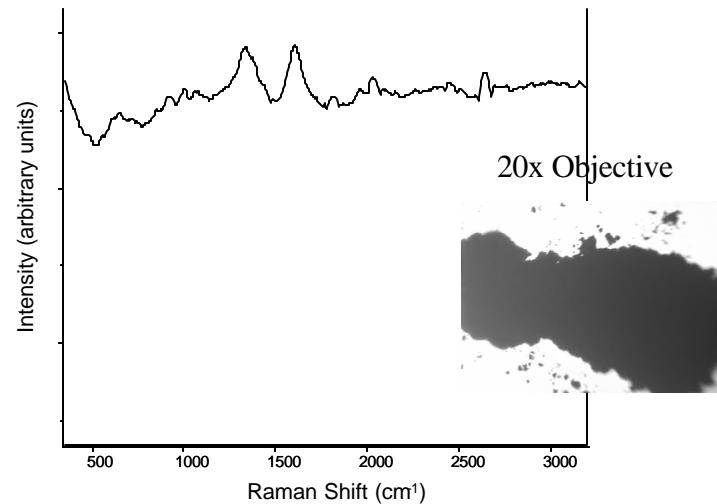


# Raman-SEM Analysis of EPA Diesel Sample

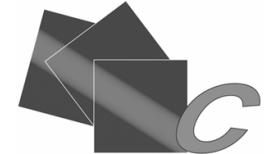
SEM, BSE and EDS



Raman Dispersive Spectra  
and Bright Field Images

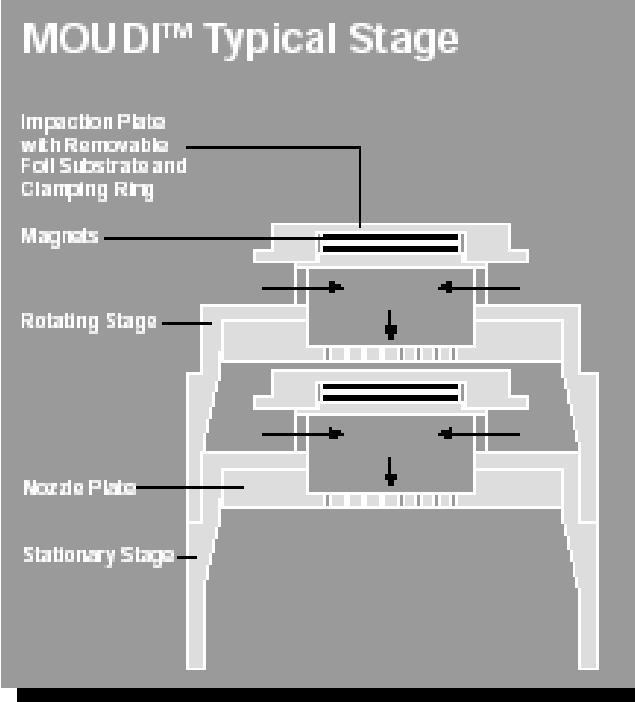


# Analysis of Individual Particles on Filter Substrate Still a Problem

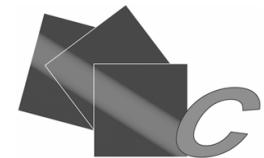


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# Micro-Orifice Uniform Deposit Impactor (MOUDI™)

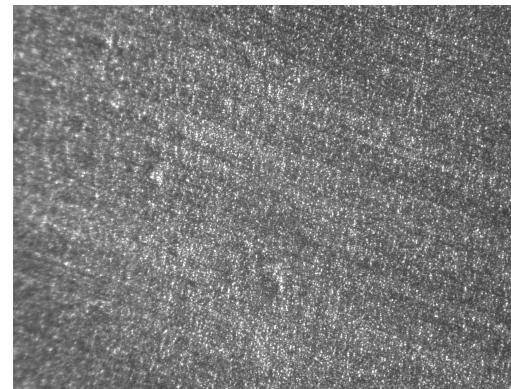
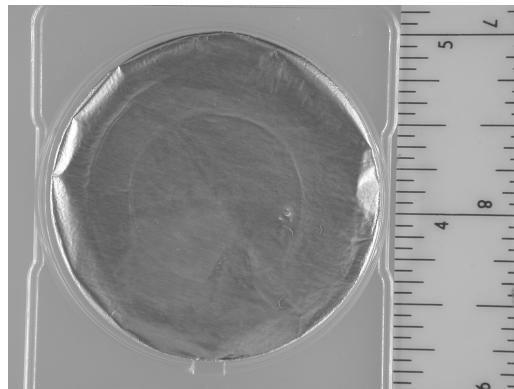


- Size-fractionate from 0.056 – 18  $\mu\text{m}$
- Obtain uniform particle deposits for chemical analyses

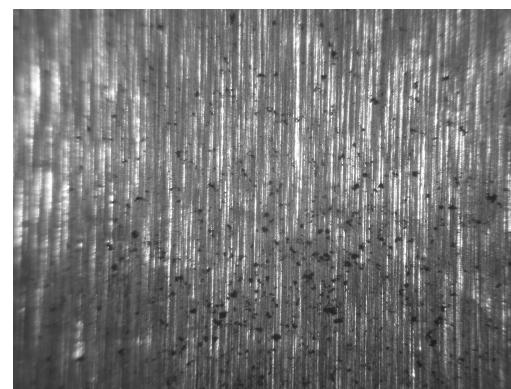
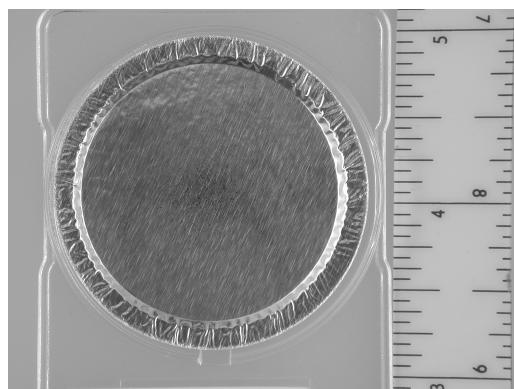


# Diesel Emissions Collected by MOUDI on Aluminum Foil

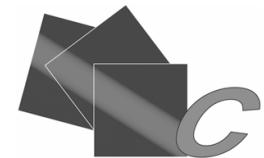
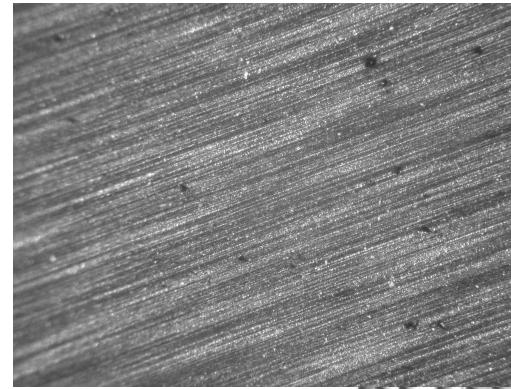
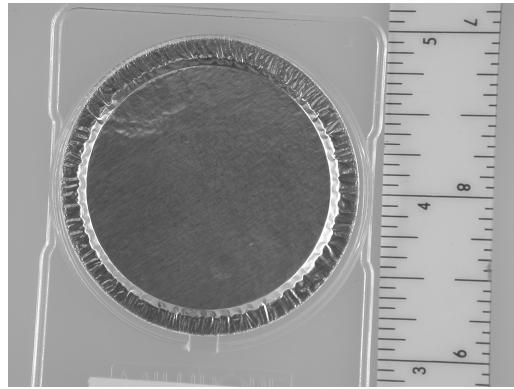
Blank Foil Cleaned  
with Alcohol



Stage 1  
3.2-18 $\mu$ m

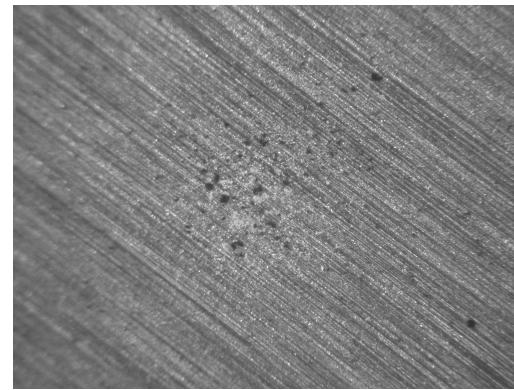
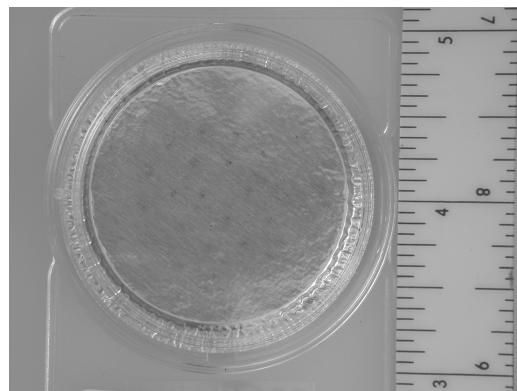


Stage 4  
1.8 - 3.2  $\mu$ m

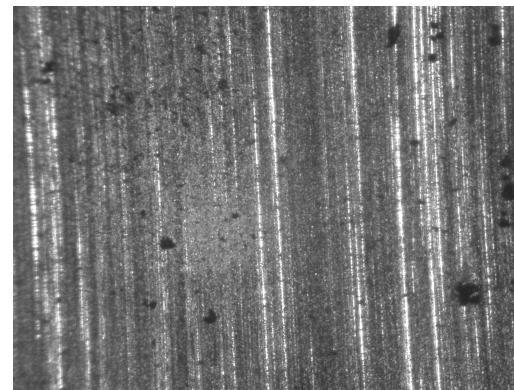
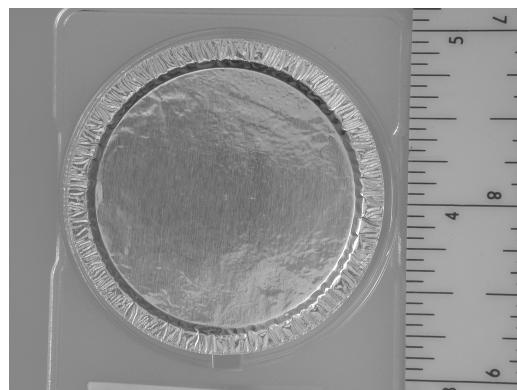


# Diesel Emissions Collected by MOUDI on Aluminum Foil

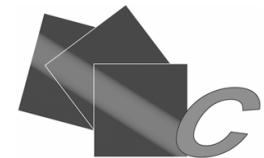
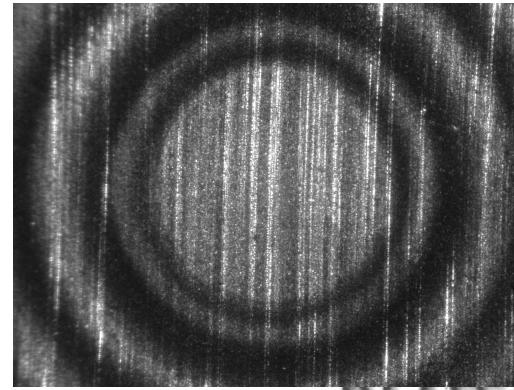
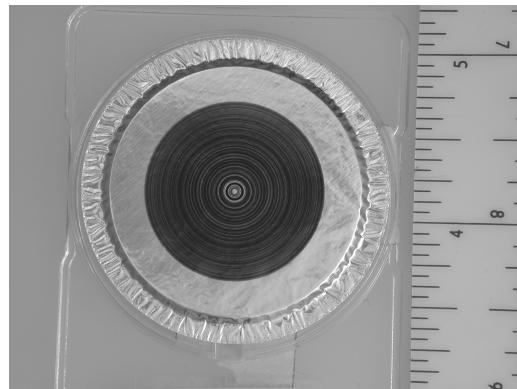
Stage 5  
0.32-1.8  $\mu\text{m}$



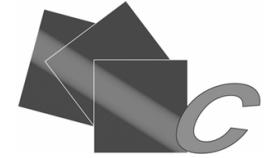
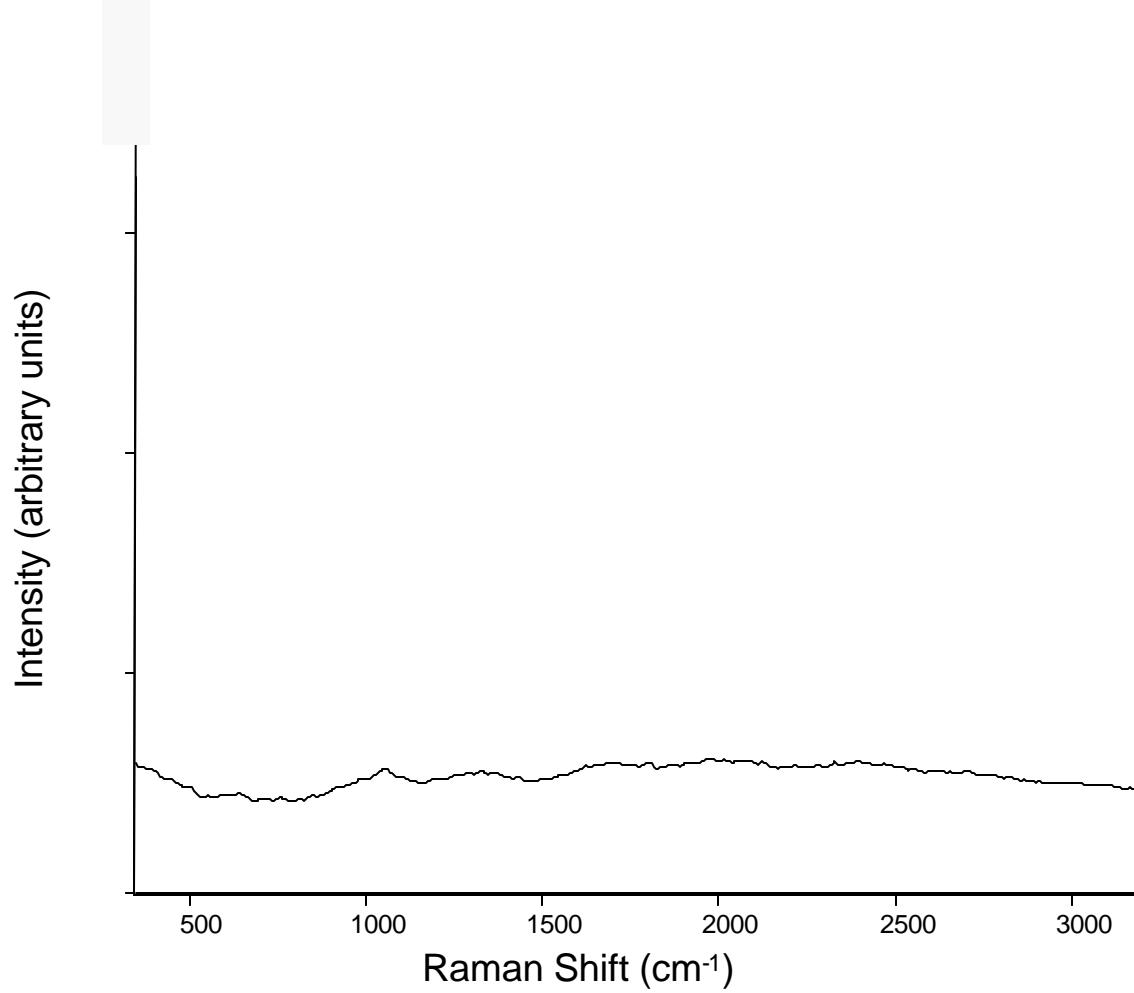
Stage 8  
0.056-0.32  $\mu\text{m}$



Stage 11  
<0.056  $\mu\text{m}$

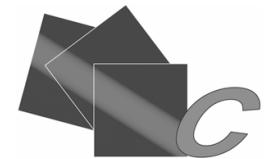
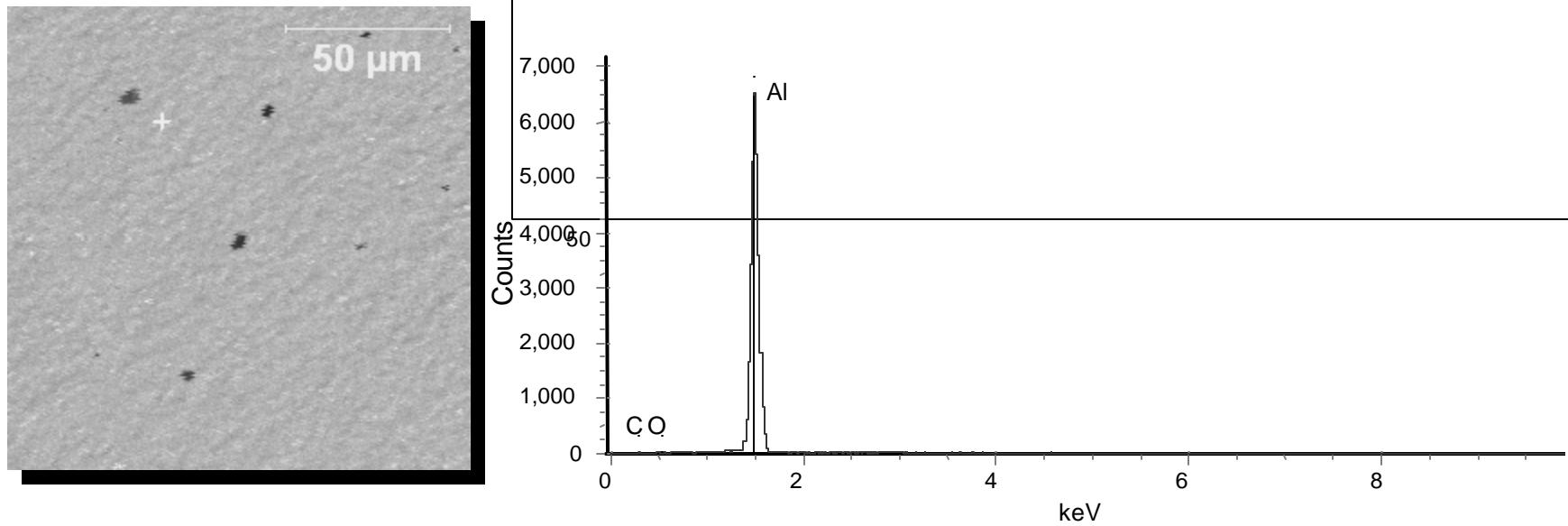


# Raman Spectrum From Blank Foil



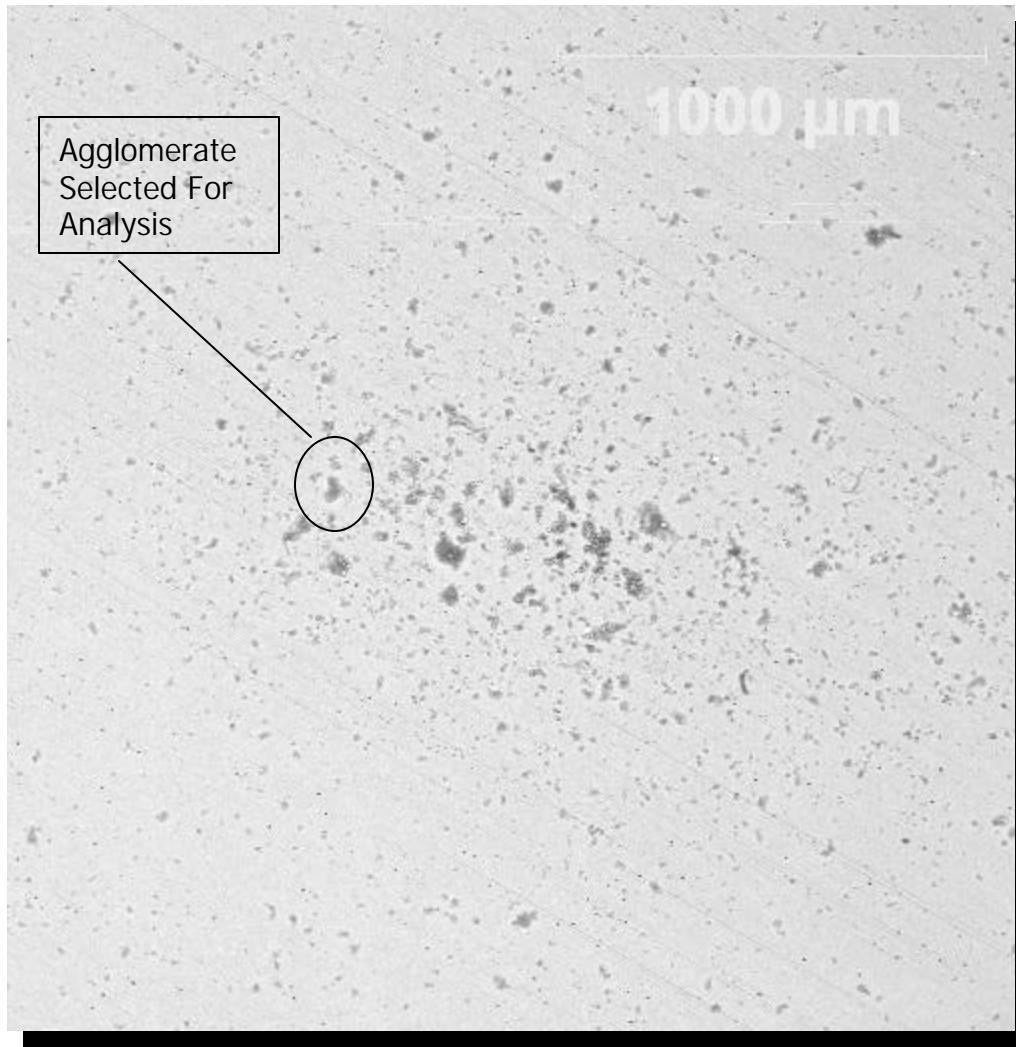
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# BSE and EDS from Blank Al Foil

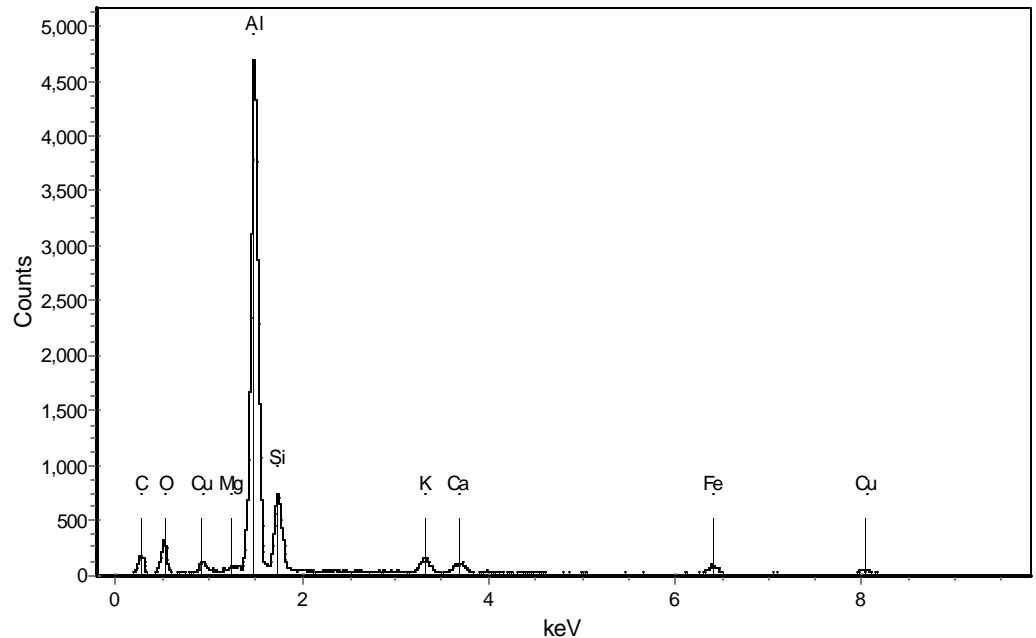
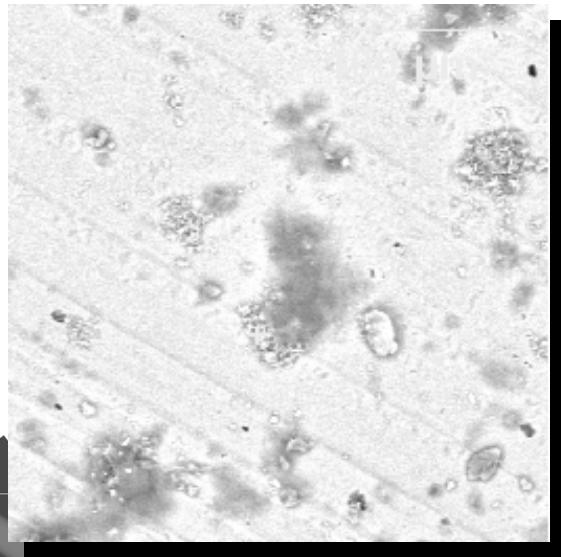
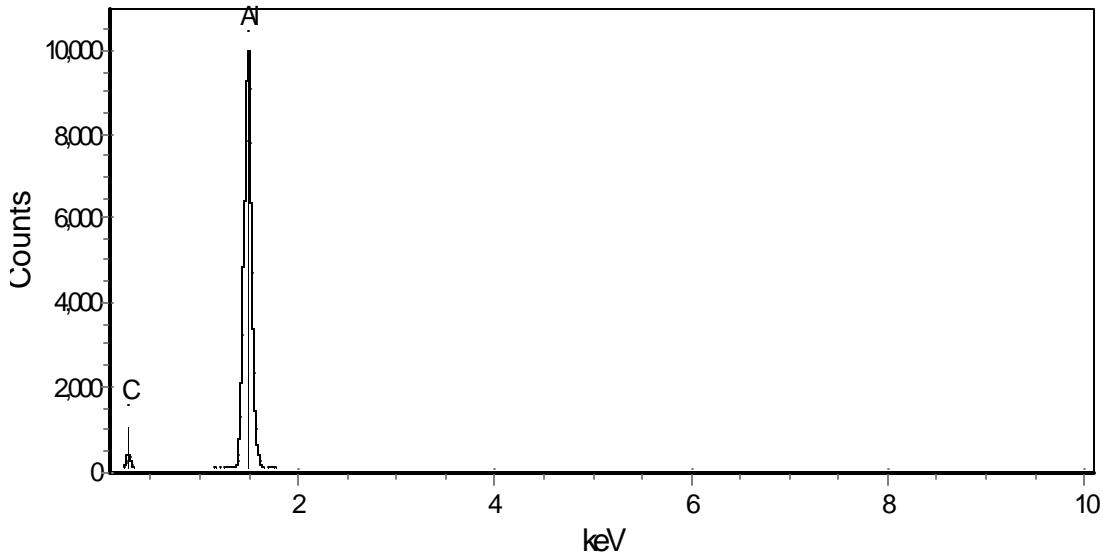
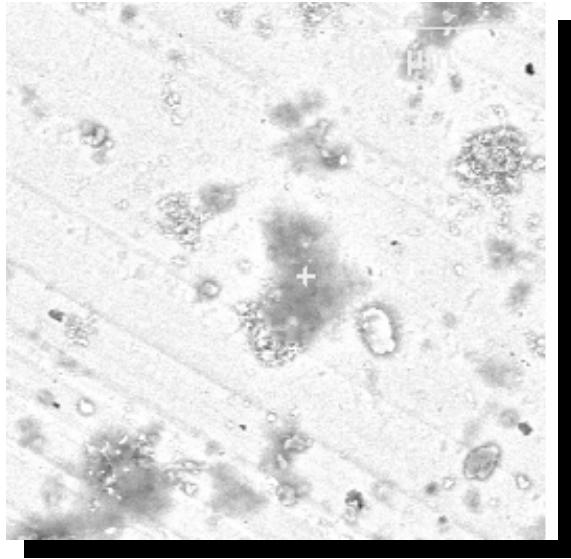


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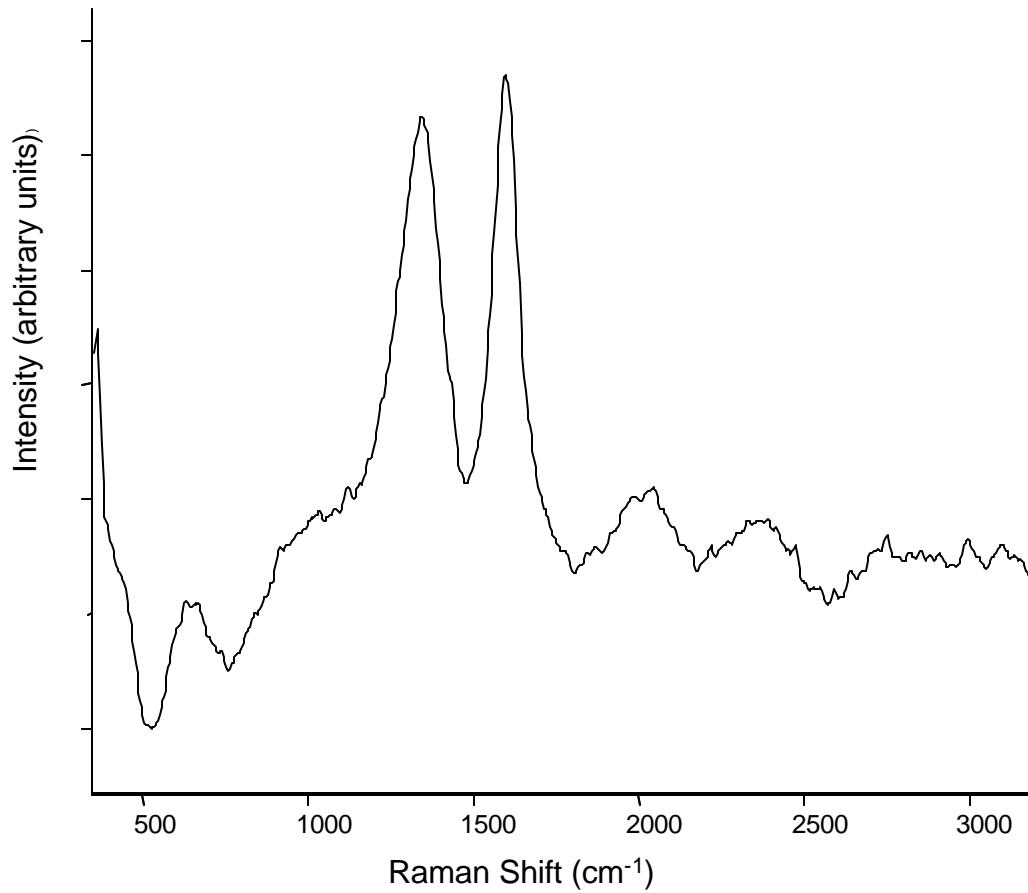
# Stage 5 Diesel - SEM Image of Jet Site



# Stage 5 Diesel – EDS from Diesel Agglomerate



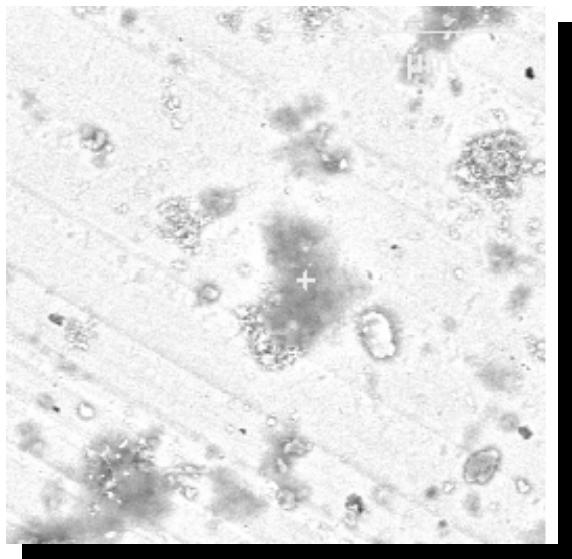
# Raman Spectrum from Stage 5 Diesel



- Collected with chamber vented
- Laser operating at 60% current
- Slit width: 100um
- Spectrometer: 300 grooves/mm

# Raman-SEM Analysis of Agglomerate

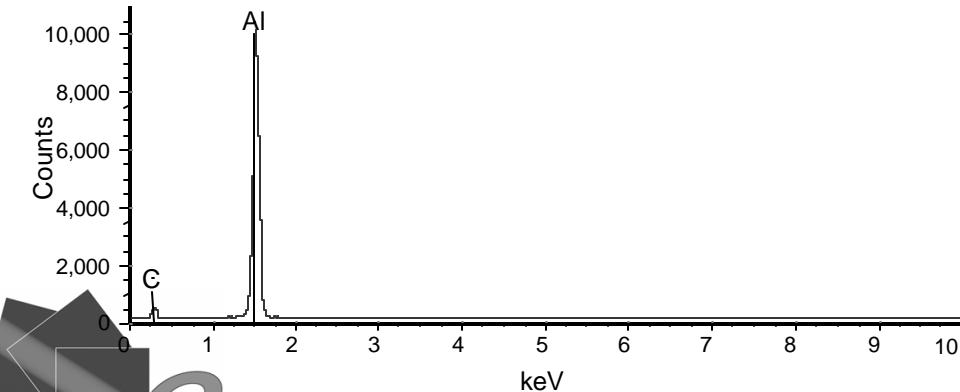
SEM BSED



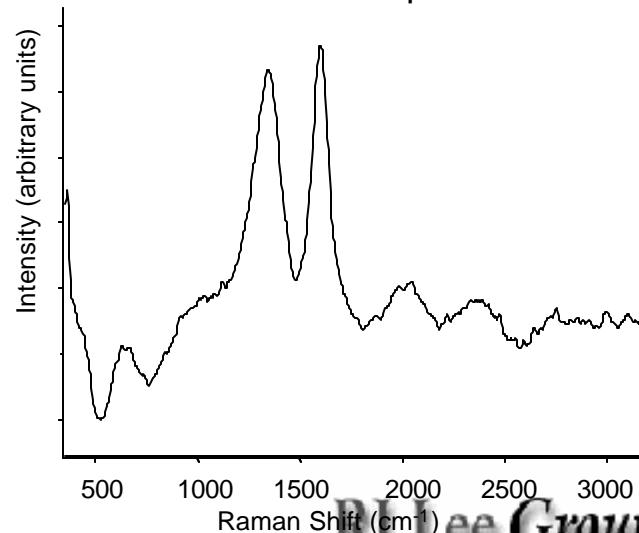
Bright Field



EDS



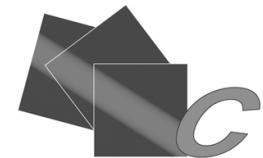
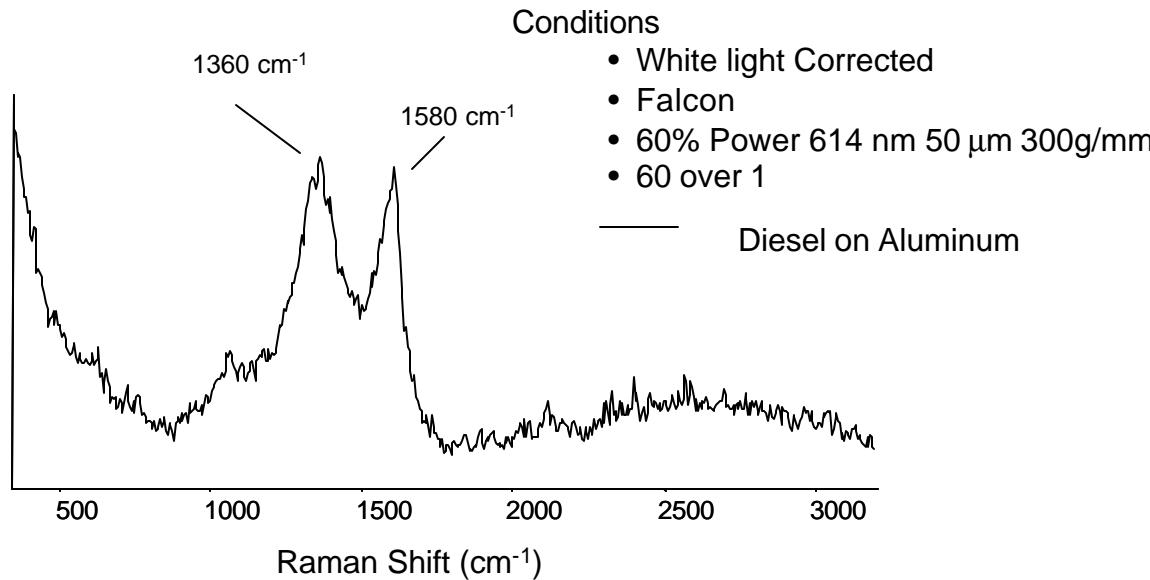
Raman Spectrum



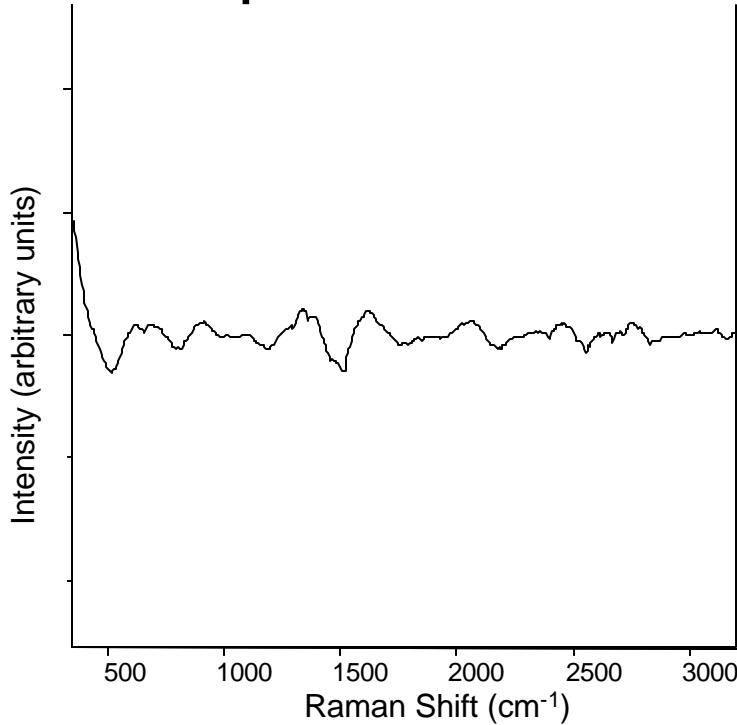
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# Raman Spectral Interpretation of Amorphous Carbon

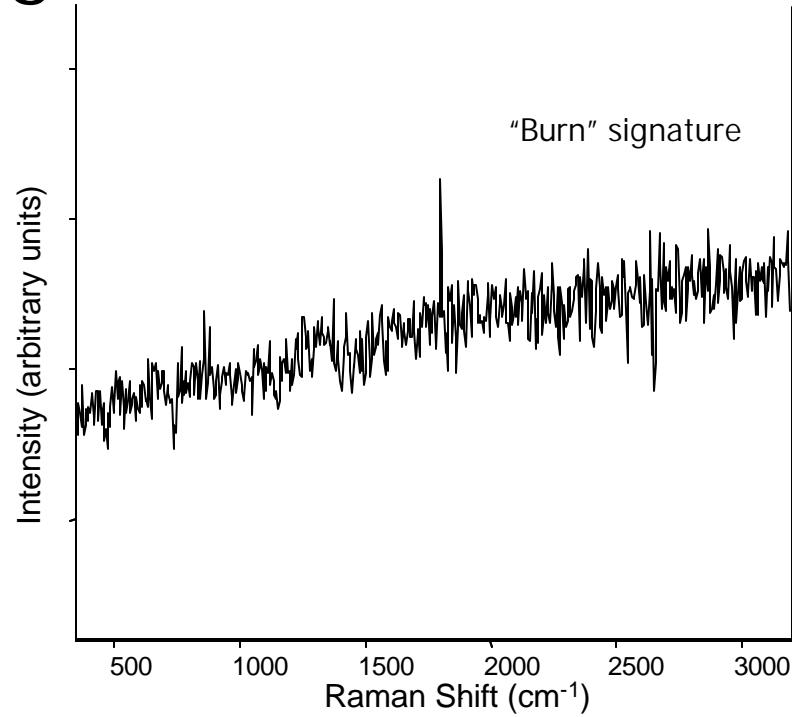
- 1360 cm<sup>-1</sup> – Carbon Sigma bond (Disorder band)
- 1580 cm<sup>-1</sup> – Graphite Band. Carbon Pi bond
- Intensity can assist with identifying the amount however there are other variables that are a function of intensity.
- Width identifies how well phonons can propagate which is a function of the order of the matrix.



# Raman Spectrum from Stage 5 Diesel in Vacuum

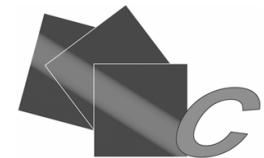


- Laser operating at **48.6%** current
- Laser power is too low to resolve diesel signature

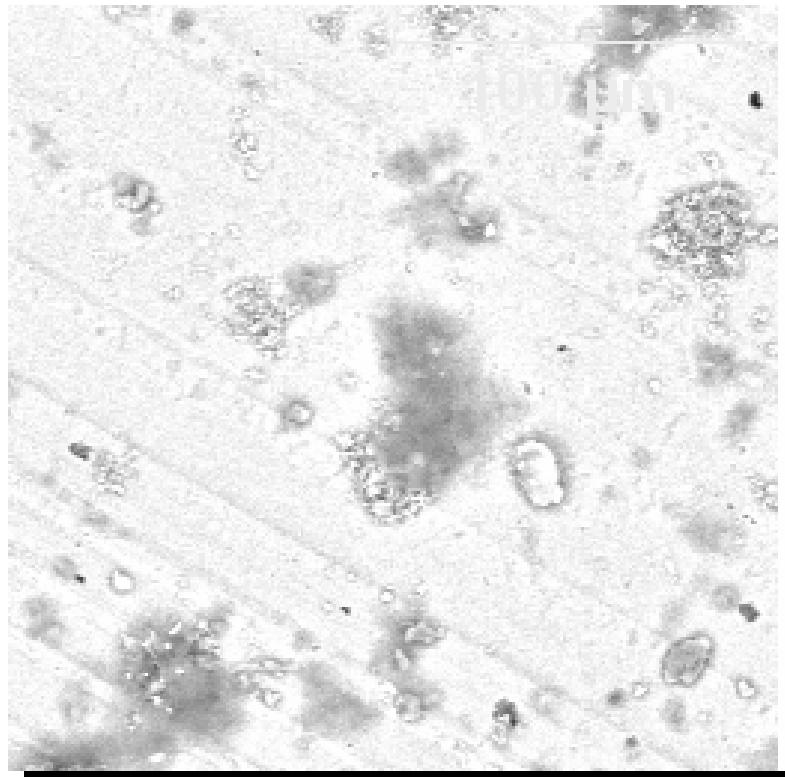


- Laser operating at **49.6%** current
- With increased laser power, sample is damaged by laser

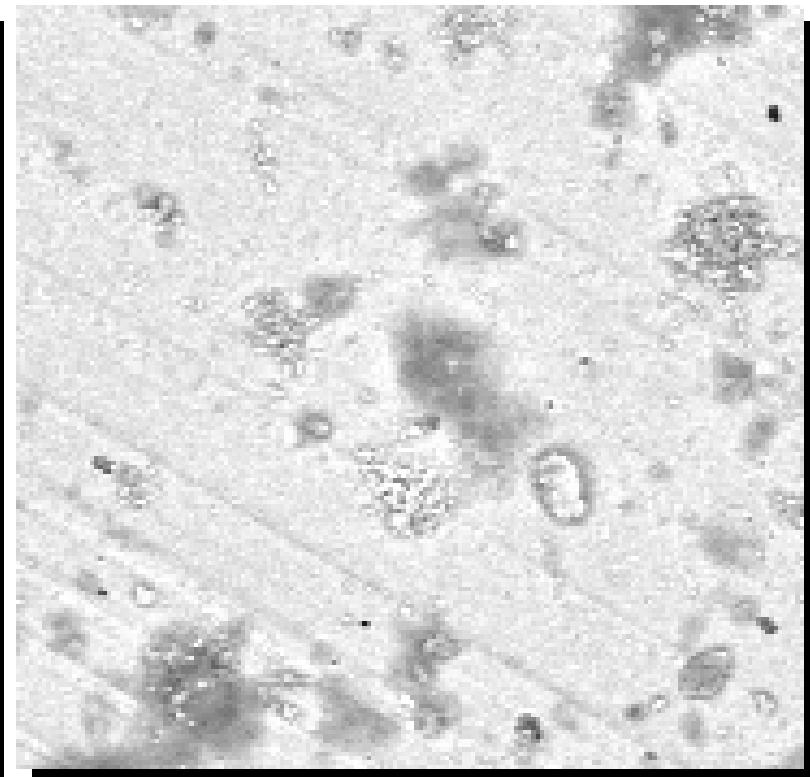
- Collected with chamber under vacuum
- Spectrometer: 100µm slit width, 300 grooves/mm



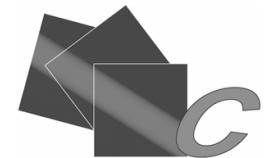
# Stage 5 Diesel – SEM Images of Agglomerate Before and After Laser Damage



Diesel agglomerate before laser exposure

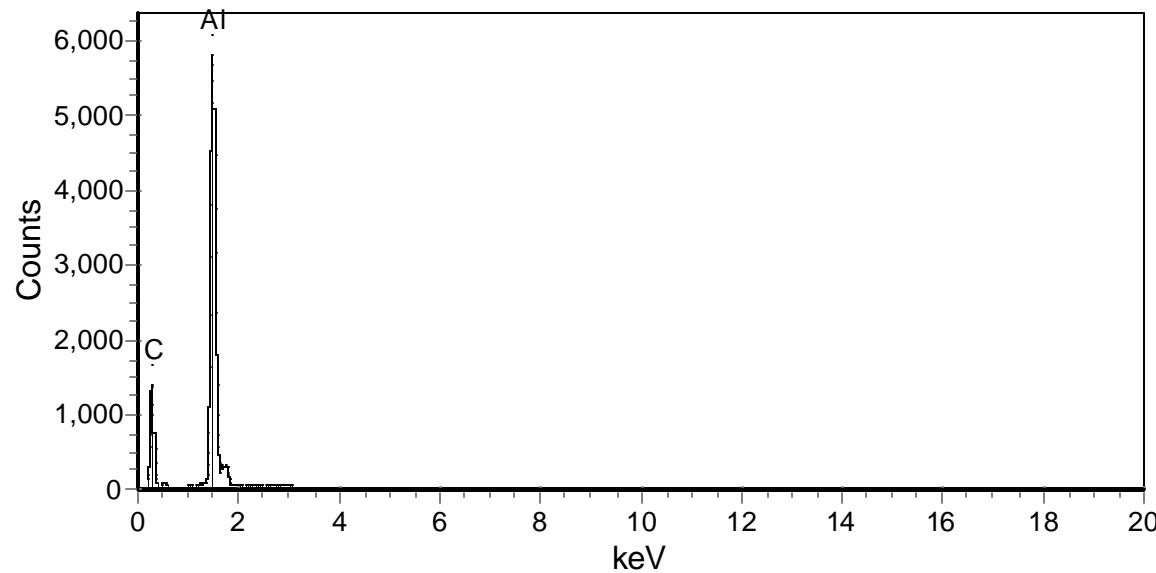
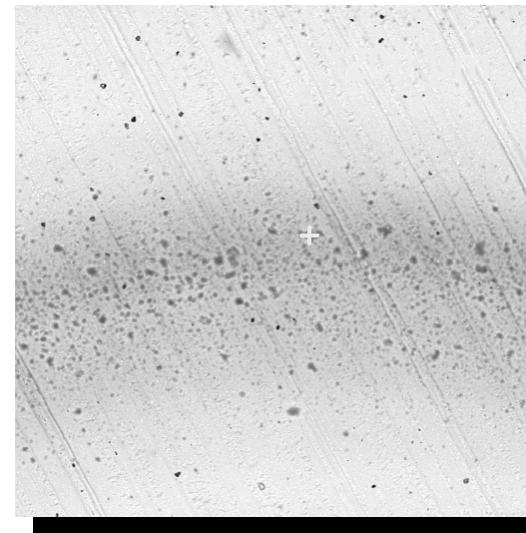
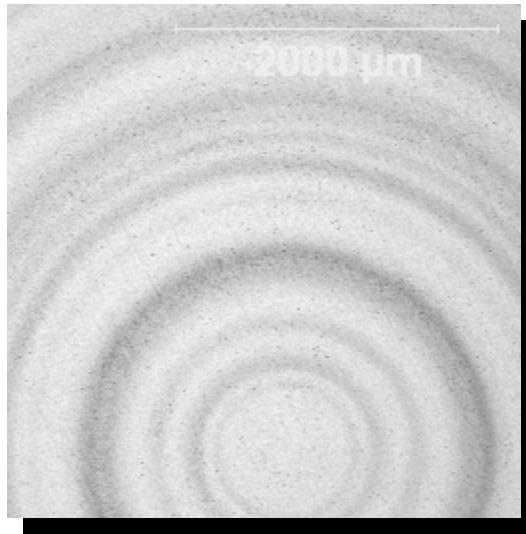


Diesel agglomerate after laser exposure



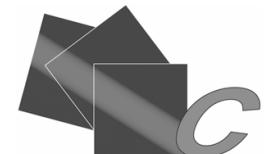
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# Stage 11 Diesel – BSE and EDS



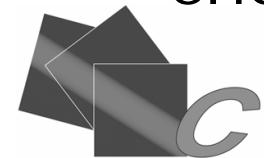
# Conclusions Diesel MOUDI Sample Analysis

- Diesel signature can be obtained from MOUDI samples using Raman-SEM.
  - BSE images, EDS, Raman (without vacuum)
- Vacuum hinders Raman analysis of these samples.
- Possible solutions.
  - Cooling stage in SEM.
  - Heavier loading on MOUDI, with no rotation.



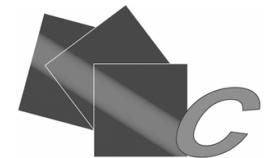
# Summary of Successes

- Designed and built a working prototype Raman-SEM instrument.
- RSEM stage can hold up to 8 samples and software controls stage rotation between SEM and Raman analysis.
- SEM, EDS spectra, Raman dispersive spectra, and Raman Chemical Images can all be obtained from the same particle.
- Analysis of diesel particulate from MOUDI sample shows feasibility of air quality analysis with RSEM.



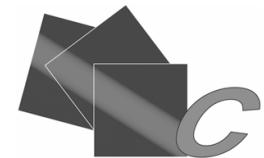
# Challenges/Hurdles

- Changing Raman Objectives
  - Objective to be used for Raman analysis must be selected and installed before sample chamber is closed.
  - If objective needs to be changed, chamber must be vented.
- Danger of Collision of Sample and Objective
  - Stage height must be set carefully before rotation to Raman to avoid collision due to small working distance.
  - All samples in chamber should be approximately the same height.



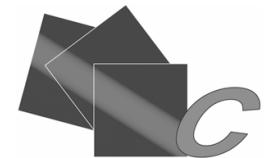
# Challenges/Hurdles

- Stage Relocation
  - Design goal was to achieve relocation reproducibility of +/- 2.5 $\mu$ m.
- Raman Bracing and Alignment
  - Rudimentary bracing of Raman stack in prototype results in optical system misalignment over time.



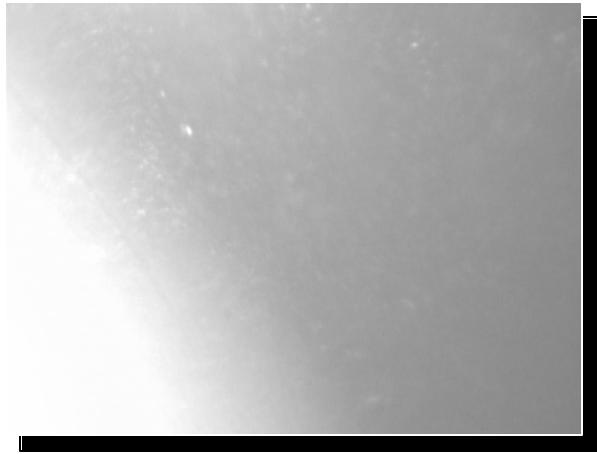
# Next Steps

- Continue and Finish Phase II Efforts.
  - Work on ambient MOUDI and filter samples.
  - Produce final report.
- Begin Phase III Component
  - Explore additional opportunities for RSEM in materials science.



# RSEM Analysis of Carbon Nano Tubes

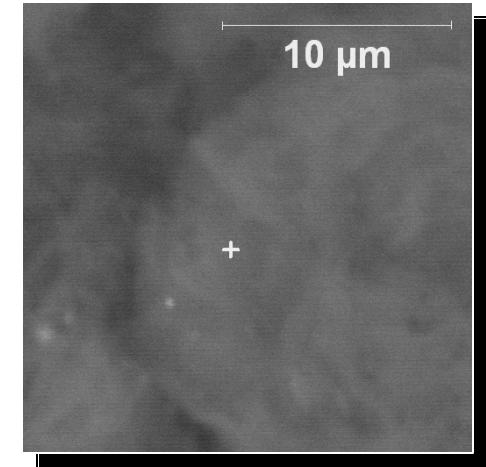
Brightfield 20x



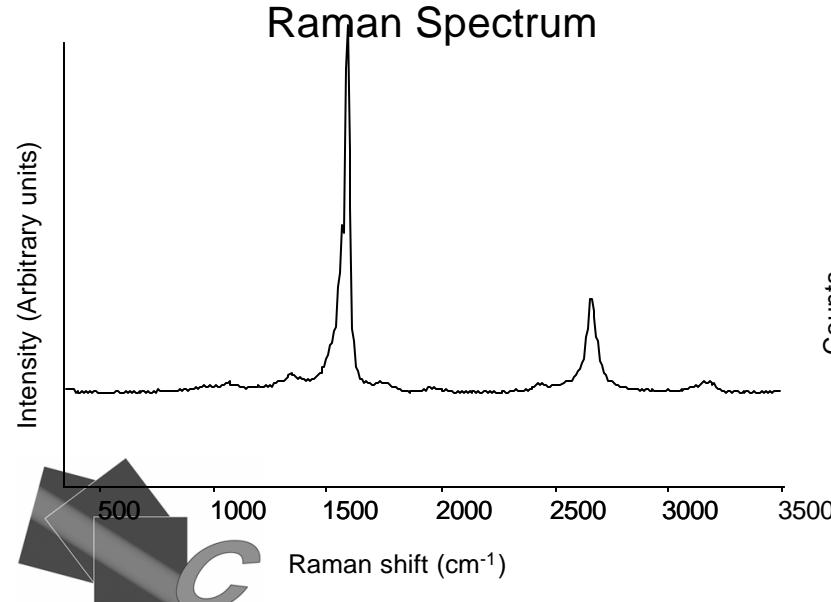
PLM 20x



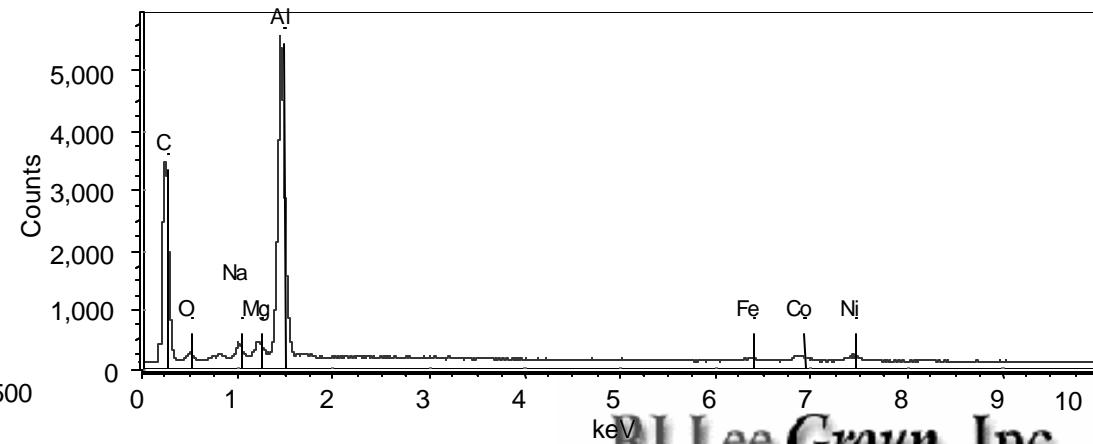
SEM 8000x



Raman Spectrum



EDS Spectrum



RJ Lee Group, Inc.